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JOURNAL

AIR POLLUTION CONTROL ASSOCIATION

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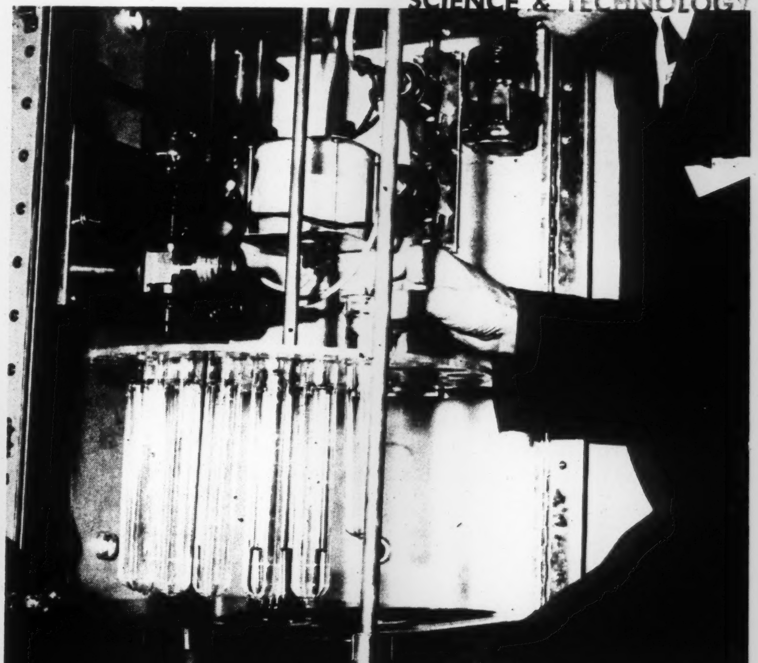

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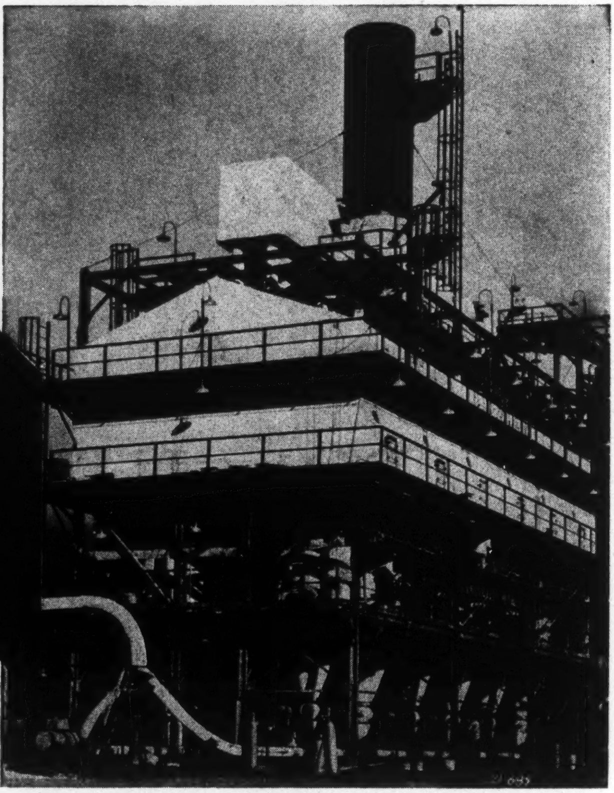
(See Page 120)



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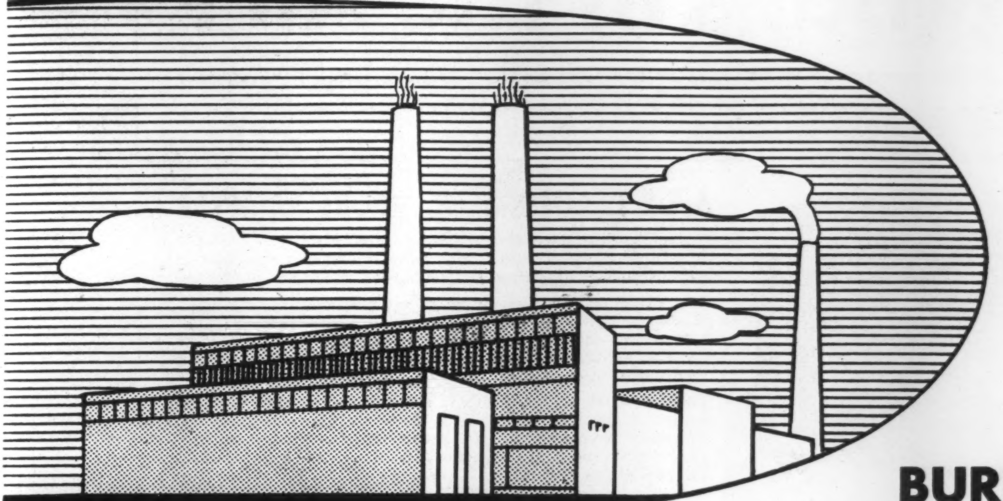

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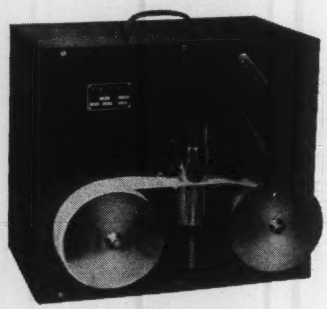

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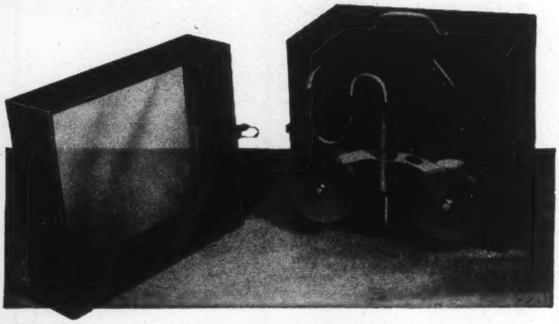

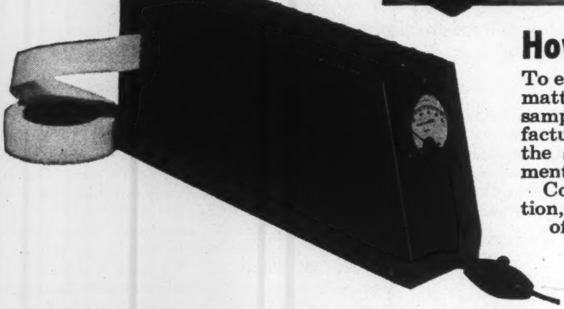

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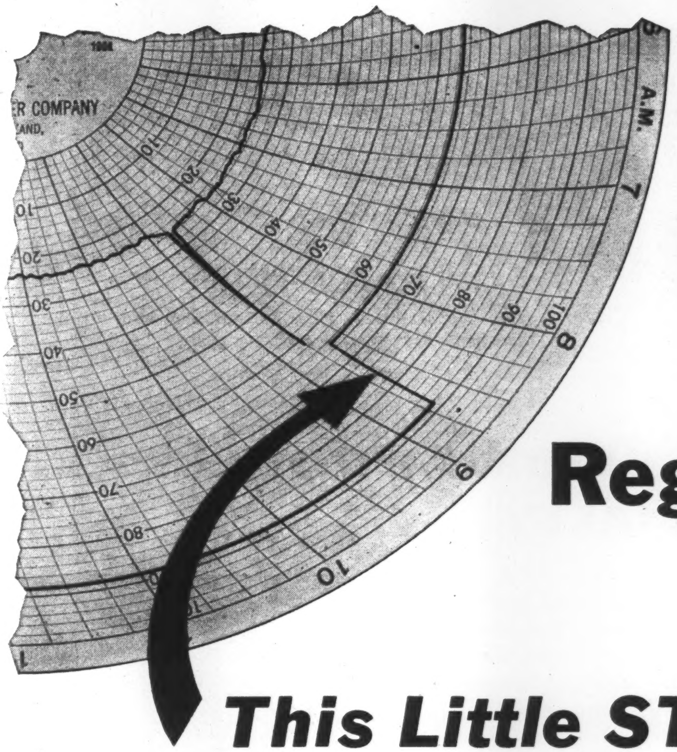

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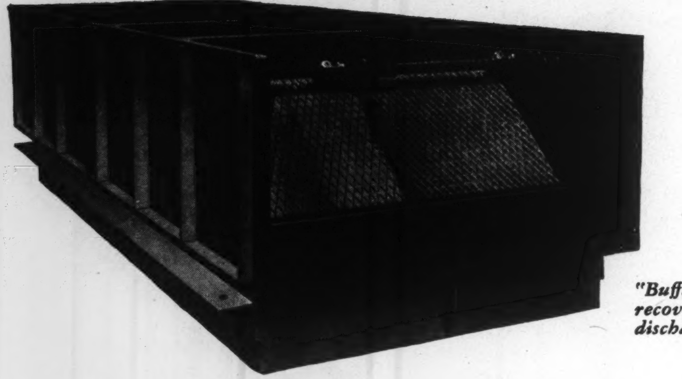

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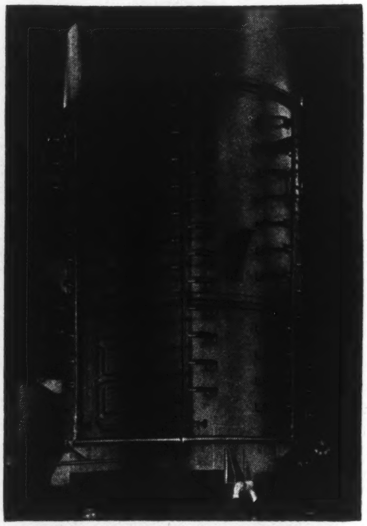

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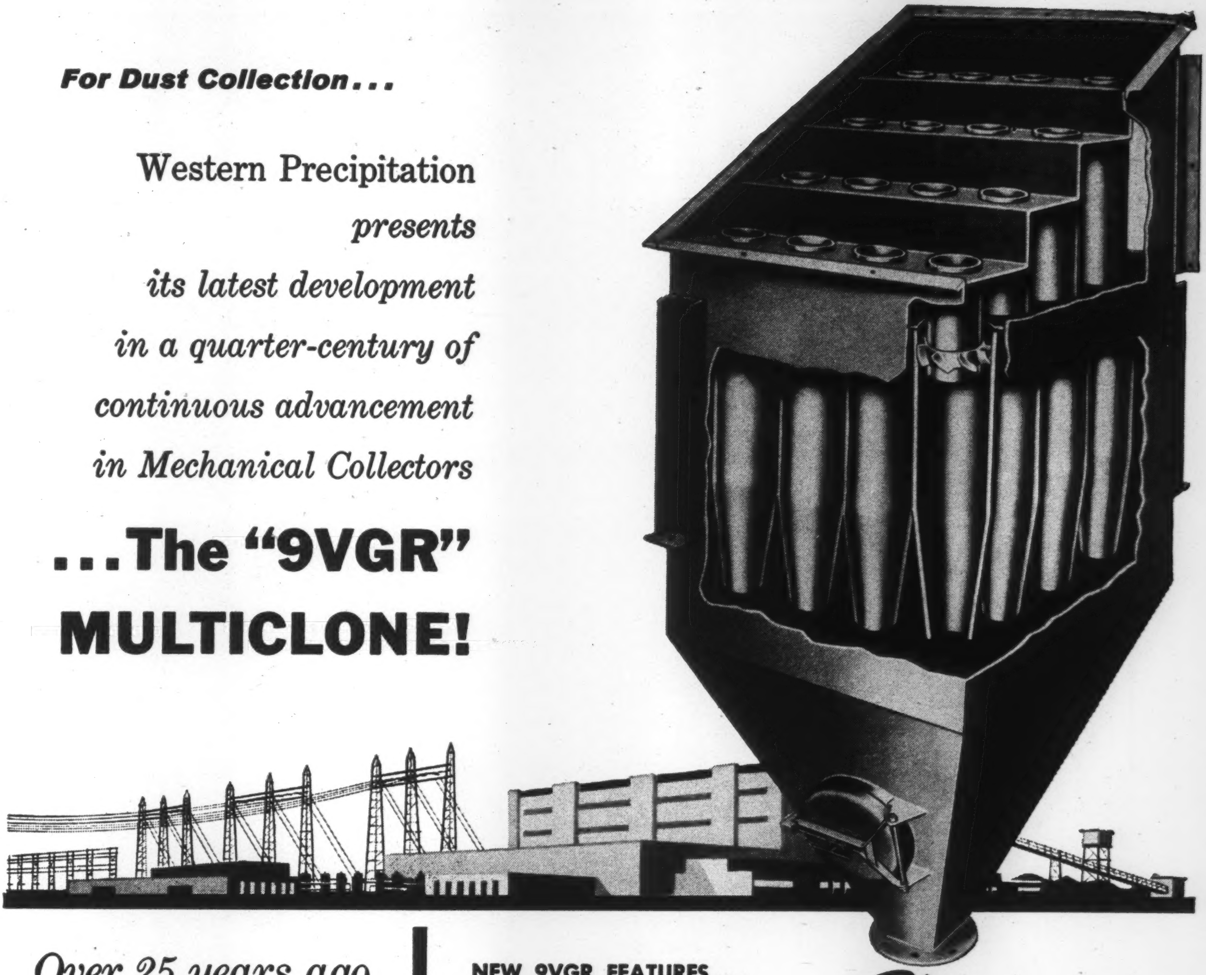

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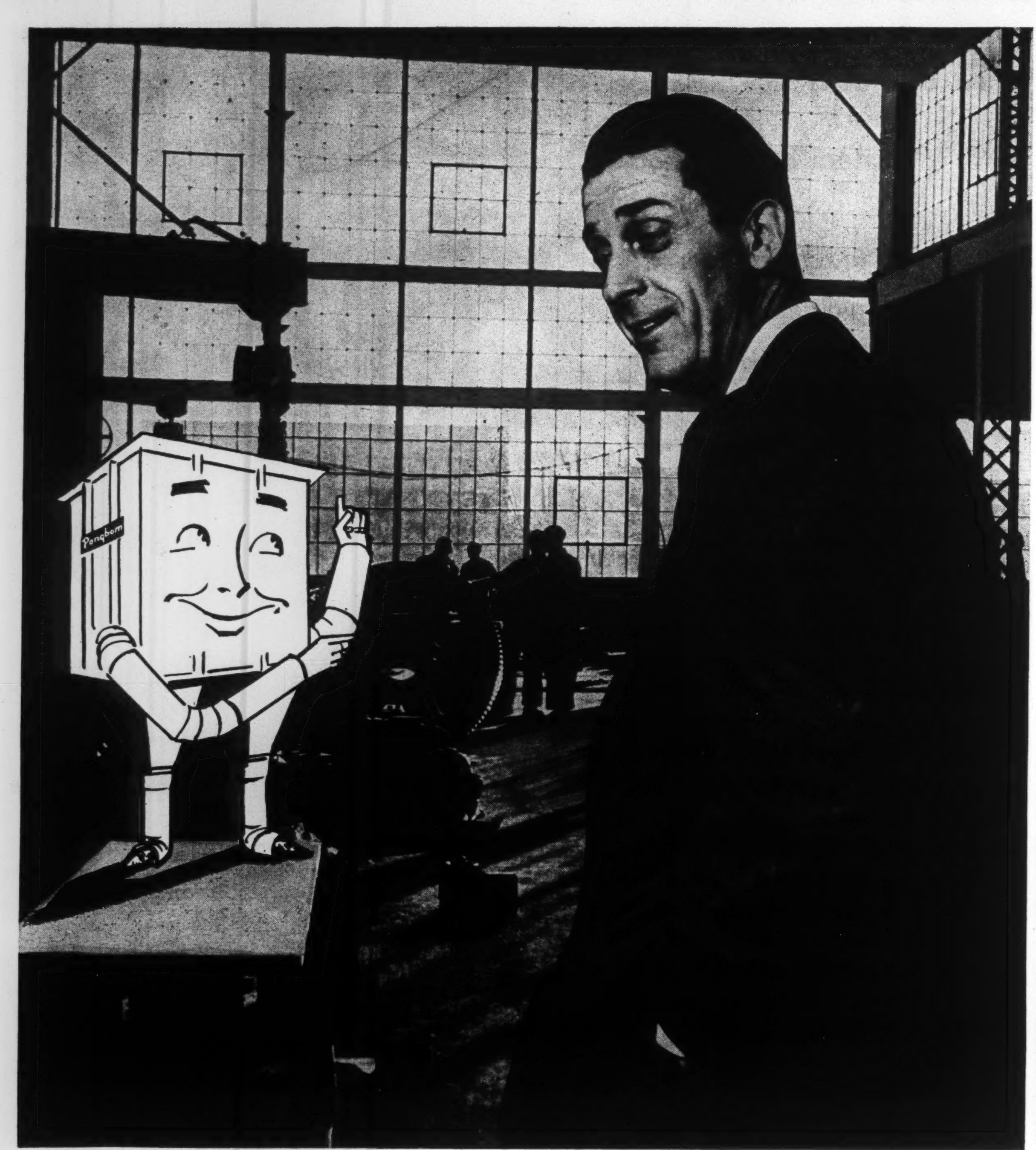

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JOURNAL OF THE AIR POLLUTION CONTROL ASSOCIATION

(Formerly "Air Repair")

A QUARTERLY JOURNAL DEVOTED TO AIR PURIFICATION

Printed in the United States
Editor: H. M. Pier
Editorial Staff: Jane M. Sumner, T. Gray
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AIR POLLUTION CONTROL ASSOCIATION
4400 FIFTH AVENUE
PITTSBURGH 13, PA.

Publications Committee 1956-57
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AUGUST 1957

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The Editor welcomes writers interested in air pollution problems and encourages them to use the pages of this journal for the expression of their opinions. But neither he nor the Association assumes responsibility for the validity of the opinions expressed herein.

THE JOURNAL OF THE AIR POLLUTION CONTROL ASSOCIATION is published quarterly at 116 East Chestnut St., Louisville 2, Kentucky, with editorial and executive offices at 4400 Fifth Avenue, Pittsburgh 13, Pa.
Application for reentry as second-class matter pending at Louisville, Ky.

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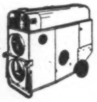

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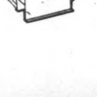

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Status Report On Auto Exhaust Control Research - - 1957*

ANDREW H. ROSE, JR. and DAVID G. STEPHAN
U. S. Department of Health, Education and Welfare
Public Health Service
Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

It is recognized that one of the more significant sources of air pollution, and one which is of continued growing national concern, is the internal combustion engine. While both gasoline and diesel engine exhausts contribute to the air pollution problem, the over-all significance of the diesel contribution is minimal because of the large ratio of gasoline to diesel fuel consumption. (1) There is, however, a local nuisance problem associated with the odor and visible smoke emission from diesel vehicles.

Research on the composition of automotive exhaust gases has indicated, in addition to solid particulates and the normal products of combustion, the presence of hydrocarbons, acetylenic compounds, aldehydes, organic acids, oxides of nitrogen, and other materials foreign to the unpolluted atmosphere. These contaminants, diluted to appropriate concentrations and irradiated with sunlight, have been demonstrated to produce typical manifestations of air pollution, *viz.*, eye irritation and symptomatic plant damage.

Areas of Research

Ideally, the attack on the solution to such a problem would be carried out in two stages:

1. The determination of the specific contaminants involved in smog formation and the establishment of threshold values as well as maximum allowable atmospheric concentrations for these contaminants.
2. The development and evaluation of control devices, equipment modifications, and /or operating techniques which would eliminate this source as an air pollution contributor.

In practice, however, the isolation of key contaminants and the determination of their respective threshold values have lagged behind the growing seriousness of the problem. Hence, a simultaneous attack on both stages has been necessary. The absence of adequate information concerning the specific contaminants involved in smog formation and the lack of data as to threshold concentrations have necessitated that control device development be based on a reduction of total contaminant discharge rather than on the elimination, or at least minimization, of specific components in the exhaust gases.

As a prerequisite to the development of a control method, average driving patterns must be determined, as well as exhaust composition and exhaust rate during each driving cycle, so that the magnitude of contaminant discharge for each operating phase may be established. On the basis of such data, the most effective control method may then be applied.

Control techniques which have been considered are modifications of fuel, changes in engine design, application of induction or exhaust devices, and the introduction of new engine principles.

Modification of Fuel

Modifications of the fuel itself are being evaluated to determine possible resultant reductions of contaminant discharge. Liquefied petroleum gas, alcohol or alcohol-gasoline blends, and low olefinic-content gasolines are being considered as substitute fuels; additives for improving the combustion efficiency of present gasolines may also be included within this category.

Change in Engine Design

Modification of engine components can produce at least partial reduction of contaminant discharges. Such modifications of a major nature include improvement in intake manifold design, recycle of exhaust gases, changes in basic carburetor design (*e.g.*, pressure carburetion), mechanical dispersion or preheating of fuel, and improvement of combustion chamber design. Further, minor modifications falling within this category are use of hotter spark plugs, reduction of valve overlap, and installation of leaner carburetor jets.

As a corollary to engine modification as a control technique, the application of optimum maintenance practices has been indicated by some data to produce significant reductions in hydrocarbon emissions. Classed in this category would be such items as proper carburetor adjustment, proper timing adjustment, minimization of blowby, and cleaning, adjustment, and necessary replacement of components of the ignition and fuel systems.

Application of Induction Devices

Mechanisms added to the intake or induction side of the engine are generally referred to as induction devices. Basically these devices are designed to limit vacuum or fuel flow during deceleration, and they include idle fuel cutoffs, throttle dashpots, and manifold vacuum controls.

Application of Exhaust Devices

Exhaust devices process the exhaust stream directly to accomplish the removal or destruction of contaminants in the effluent gas. Principles employed here are generally afterburning, catalytic oxidation, absorption, adsorption, filtration, condensation, electrostatic precipitation, and chemical neutralization.

Introduction of New Engine Principles

A final possibility is the introduction and acceptance of new engine principles. Often mentioned are fuel injection engines and gas turbines.

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*Presented at the 50th Annual Meeting of The Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

Present Status of Research

Organizations of widely diversified interests have contributed to the work accomplished to date in automotive emission control. Groups involved include air pollution enforcement agencies, research institutes, universities, the automotive and petroleum industries, numerous private companies and individuals, and agencies of the Federal Government.

Enforcement Agencies

Perhaps the organization most crucially concerned with the auto exhaust problem is the Los Angeles County Air Pollution Control District, since in the Los Angeles area alone have smog episodes, ascribed to the previously mentioned photochemical reactions, occurred with regularity. Much of the preliminary work in the field of auto exhausts has been performed by Los Angeles County. (While not having undertaken specific research projects, it is of interest to note that other local enforcement agencies, *e.g.*, in Cincinnati, Ohio and New York City, N. Y., recently have shown increased interest in the curtailment of engine exhausts.)

Work by the Los Angeles County Air Pollution Control District has resulted in estimates of the actual rates of exhaust discharge from automobiles during each cycle of their operation. (2) Analyses, again made during individual operating cycles, have indicated the exhaust concentrations of carbon monoxide, carbon dioxide, and oxygen, and the concentrations of groups of components such as hydrocarbons, acetylenic compounds, oxides of nitrogen, and lower aldehydes. (2) Measurements of particulate emission rates have also been made. (3) In addition, a study was made of the average Los Angeles driving pattern in which the percentage of total driving time for each driving cycle (acceleration, cruise, deceleration, and idle) was determined.(2) From the above data, assessment of the total automotive emissions to the Los Angeles atmosphere has been made. (4) Also, in March of this year, a Conference on the Catalytic Decomposition of Vehicular Exhaust was sponsored jointly by the District and the Air Pollution Foundation. At this closed conference, papers were presented on the causes of smog, (5) the relationship of auto exhaust to smog, (6) the legal aspects of exhaust control, (7) the capabilities and limitations of oxidation catalysts for organic matter, (8) and the use of catalysts to decompose nitric oxide in auto exhaust. (9)

The present automotive exhaust research program of the Los Angeles County Air Pollution Control District consists of three phases: (10) (1) basic research, (2) evaluation of total pollution, and (3) testing of proprietary devices.

Basic research projects which are being conducted by the Los Angeles County Air Pollution Control District are:

(1) Relationship between fuel compositions and their smog-forming capabilities. (Preliminary report presented March, 1957) (11)

(2) Effect of fuel composition on the composition of exhaust.

(3) Effect of compression ratio on the formation of oxidants.

(4) Catalytic decomposition of exhaust hydrocarbons.

(5) Catalytic decomposition of oxides of nitrogen.

(6) Analysis of vapor and gas phase photochemical reactions of types possible in exhaust mixtures.

(7) Determination of the ratio of formyl compounds in smog produced by auto exhaust.

(8) Combustion conditions conducive to formation of oxides of nitrogen.

(9) Sources of hydrocarbon emissions other than those from the idle circuit.

(10) Engine conditions as related to exhaust composition.

(11) Use of LPG in relation to exhaust composition.

Studies constituting the evaluation of total pollution, which are either in progress or under consideration, involve a reassessment of the average driving pattern in Los Angeles County, the measurement of average evaporation losses from automobiles, and the establishment of ideal maintenance standards for Los Angeles automobiles.

The program of the Los Angeles County Automotive Combustion Laboratory to date has dealt primarily with the testing of emission control devices. Such mechanisms include catalytic mufflers, afterburners with and without ignition devices, deceleration fuel shut-offs, manifold vacuum breakers, manifold vacuum limiters, carburetor isolating valves, gasoline additives to promote combustion, ozone generators to promote combustion, catalysts to promote combustion, carburetors of new design, various atomizers and vaporizers, and exhaust scrubbers and filters. A report on the status of induction devices tested by this laboratory was recently presented. (12) This work will continue to be an important part of the Automotive Combustion Laboratory program. Initial testing has been done with a dynamometer engine, but, as devices approach final development, Los Angeles County authorities believe that road testing must supplement the dynamometer test work. To date, no device has been approved by the Los Angeles testing laboratory as being acceptable for the control of automobile exhaust emissions.

Research Institutes

Research organizations such as the Air Pollution Foundation, Southwest Research Institute, Stanford Research Institute, Midwest Research Institute, Armour Research Foundation, and the Franklin Institute have done work in this field. At research institutes, studies have been completed concerning automobile exhaust particulate discharge, (13) the composition of auto exhaust and its photolysis products, (14) evaluation of catalytic exhaust converters, (15) feasibility studies of control methods for automobile exhausts, (16) effects of hydrocarbon type on eye irritation and oxidant formation, (17) eye irritation from irradiated auto exhaust, (18) and reactions of auto exhaust in sunlight. (19)

A field evaluation of a catalytic exhaust converter, performed early in 1955, (15) led to the conclusion that the catalytic muffler studied, in its present embodiment, is not sufficiently rugged and long lived for use as a partial solution to the Los Angeles smog problem. A feasibility study of a number of exhaust control methods was also carried out in 1955. The report on this subject evaluates economically the proposed stop-gap procedures for solution of the exhaust problem and reviews the status of proposed control devices.

Projects currently in progress at the various research institutes involve studies of the composition of exhaust gases, (20) studies of the effect of exhaust gas on plants and on rubber cracking, (20) studies of the reactions of people to irradiated and non-irradiated exhausts, (21,22) and studies to determine what reduction in exhaust contaminants is needed to reduce smog markedly and whether a concurrent reduction in oxides of nitrogen emission is required. (23)

Universities

A great deal of the work on fundamental air chemistry and the smog reaction has been done by the universities and their research foundations. However, work on the control aspects of the auto exhaust problem has not been so widespread at the academic level. The California Institute of Technology and the University of California at Los Angeles apparently are the only two universities which have entered this field. At present, air chemistry work is continuing, including basic studies of oxygen-nitrogen reactions. (24) A new air resource test facility for auto exhaust work is being built (25) and emission control work is now proceeding along at least three lines: afterburner studies, development of an exhaust scrubber, and use of water injection to alter exhaust gas composition. (25)

Automotive and Petroleum Industries

Research laboratories of the automobile and petroleum companies have been studying the internal combustion engine air pollution problem since the 1920's. This work was done by individual companies and dealt primarily with carbon monoxide, toxic lead compounds, and visible smoke. However, no concerted action by industry was taken until the arrival of *smog* in the Southern California area. At present, the automotive and petroleum industries, through the Coordinating Research Council and the Automobile Manufacturers Association, are continuing to do research on automotive exhausts. Findings are pooled on a noncompetitive and non-profit basis through a cross-licensing agreement similar to that employed in the development of the sealed-beam headlight.

The Coordinating Research Council has two sustaining members, the Society of Automotive Engineers and the American Petroleum Institute; the Council coordinates joint research endeavors of the automotive and petroleum industries to integrate fuel development with vehicle design. The Automobile Manufacturers Association, on the other hand, is a trade association of the automobile industry alone. Engine exhaust studies by the CRC and the AMA are interrelated through numerous joint committee memberships.

Projects conducted by the automotive and petroleum industries to date have included: (26,27)

(1) Development of a mobile, continuous infrared analyzer for engine exhausts.
(2) Development of instruments for measuring total intake air to an automobile engine.
(3) Design and evaluation of numerous induction devices.
(4) Performance of a preliminary field survey of 50 automobiles in the Los Angeles area to determine exhaust compositions, exhaust rates, driving patterns, etc.
(5) Execution of a survey of the exhaust-control literature.
(6) Studies of the effect of engine modifications and fuel composition on exhaust characteristics.
(7) Preliminary testing of a number of proposed exhaust conversion catalysts.
(8) Studies of flame quenching in the cylinder and its effect on unburned hydrocarbon emission.
(9) Testing of proprietary control devices.
(10) Estimation of the magnitude of hydrocarbon and oxides of nitrogen emissions from auto exhausts in the Los Angeles area.
(11) Calculation of the percentage contribution of each driving cycle to the total hydrocarbon emission from auto exhausts.
(12) Determination of the source of hydrocarbon emission during deceleration when the idle fuel supply is cut off.
(13) Conduct of two traffic surveys in the Los Angeles area (May, 1956 and January, 1957) to determine driving patterns on the basis of both manifold vacuum and actual car motion.

In November and December, 1956 an extensive field survey was conducted in the Los Angeles area.(28) A sufficient number of automobiles were chosen, on a statistical basis, so that results of exhaust analyses and rate measurements, and determination of average driving patterns will be known with a 95% confidence level. Results of this survey are now being analyzed. (27) If, based on these tests, it is determined that a manifold vacuum control device effective during the deceleration cycle will result in a satisfactory reduction of hydrocarbons, it is anticipated that such devices can be furnished by the auto industry as accessory equipment. (27)

Probable next areas of investigation by the Coordinating Research Council (29) will be, first, studies of the oxides of nitrogen, including development of analytical instrumentation and research on the operating conditions affecting emission of these compounds, and, second, studies of how fuel, lubricant, engine, and operating variables affect emission of specific organic components. The rapidity with which these programs will be pursued, however, will depend upon the development of appropriate analytical techniques and upon the final apportionment of responsibility of specific organic compounds for smog formation.

Research areas which are now being expanded by the CRC (29) are, first, studies of the effects of maintenance practices on exhaust emissions, and, second, studies of the effects of existing component modifications (*e.g.*, leaner fuel jets, hotter spark plugs, reduced idle settings, *etc.*) on exhaust. The CRC is also supporting research by the U. S. Bureau of Mines on development of exhaust analysis techniques. (27)

Three current study areas which are to be expanded by the Automobile Manufacturers Association in the coming year are: (26)

(1) Development of both catalytic and non-catalytic exhaust control devices.
(2) Design and development of production models of induction devices.
(3) Application studies dealing with modification of existing engine components.

The Ethyl Corporation and the Western Oil and Gas Association have also recently reported work on the effect of tetraethyl lead on smog(30) and effects of fuel composition on auto exhaust (31) respectively.

Private Companies and Individuals

Development of control devices has been undertaken by a number of private companies as well as by individuals. These companies are primarily carburetor suppliers, catalyst manufacturers, and firms organized solely for the manufacture and sale of such devices. Understandably, information developed by private companies and individuals on proprietary control devices is rarely published and is not readily available. Papers have been presented in the last several months, however, concerning both catalytic mufflers (32) and direct-fired afterburners. (33)

It is known that a large number of control devices have been invented, (10,34,35,36,37,38,39) but none as yet are known which have been found to be completely satisfactory on testing. (10,15,16,17,26) Idle fuel shutoffs and manifold vacuum controls are common among these devices. Others include improved carburetor designs, additives, exhaust recycle systems, afterburners, and catalytic mufflers. Several companies are working on catalyst development for use in exhaust converters and at least one concern is now developing container materials for catalytic mufflers.

Agencies of the Federal Government

Through research grants and contracts with research organizations and individuals and through interagency fund exchanges, the Public Health Service has contributed to the research effort dealing with the automotive exhaust problem. The U. S. Bureau of Mines and the U. S. Bureau of Standards are both performing work under this latter funding arrangement. These government agencies are conducting or sponsoring work in several fields. Work is now in progress on the development of methods for identifying and quantitatively measuring almost any individual constituent of internal combustion engine exhaust. (40) Emphasis is on the identification and quantitative determination of hydrocarbons and oxygenated compounds. To make analytical techniques less expensive, less complex, and simpler to operate, such techniques as vapor-phase chromatography are being accentuated rather than mass spectrometer procedures.

With the development of analytical methods, studies will be undertaken to relate exhaust composition to fuel composition and additives. (40)

Since particulate matter represents one route by which hydrocarbons and other substances are released to the atmosphere, and since particulates may exert effects quite different from those of gases, an investigation of particulate emissions from automobile engines is now under way. (41)

Lastly, a project is being conducted concerning the application of an electrostatic precipitator used in conjunction with radio-active treatment of automobile exhaust streams. (42)

Discussion

The expressed urgency for a solution to the air pollution problem has made mandatory a simultaneous attack on both the basic causes of air pollution and the development of control techniques. While this procedure is a deviation from the ideal, it has become the only reasonable approach to an early alleviation of a condition which has the potential of becoming critical in certain areas. As a consequence, presently proposed automobile exhaust control techniques have been developed on the basis of a reduction of total cotaminant discharge, without giving consideration to the effects of singular components of the discharge. Increased research on more basic aspects should, therefore, provide the groundwork for more effective control development. At this time data indicate two specific groups of chemical compounds, namely oxides of nitrogen and olefinic hydrocarbons, contribute to the formation of smog. Emphasis to date has been on control of the hydrocarbons, but it is now felt that work on oxides of nitrogen should be accelerated.

While preliminary studies have inferred that over 60% of the total emission from auto exhausts occurs during deceleration, (43) more recent but as yet unverified work. (26,29) indicates that the magnitude of the contribution of the deceleration cycle may not exceed 30-35% of the total. Such a revision of background data could reduce the expected effectiveness of induction devices for the overall reduction of automobile exhaust contaminants. Confirmation of these more recent data could, therefore, seriously delay the satisfactory application of control devices, since the short-range emphasis on equipment development has thus far been on induction devices.

Proposed Federal Action

The Public Health Service has initiated and is continuing to maintain liaison with the Automobile Manufacturers Association, the Coordinating Research Council, and the Los Angeles County Air Pollution Control District regarding their progress in the automotive exhaust research field. In addition, plans are under way for a Public Health Service-sponsored Conference on the Automotive Exhaust Air Pollution Problem, scheduled for October 3-4, 1957. The objectives of this Conference will be to discuss, from both technical and administrative standpoints, the testing protocols which are necessary in the evaluation of exhaust control devices, to critically evaluate present and proposed sampling and analysis techniques for auto exhaust, and to set forth those definitions in the field in need of standardization, coming to agreement if possible on them. If necessary, the group will constitute themselves an ad hoc committee to complete consideration and accomplishment of these objectives.

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Determining Organic Vapor Concentration In Air

H. L. BARNEBEY and W. L. DAVIS
Barnebey-Cheney Company, Columbus, Ohio

The effect of man-made and natural pollutants in air even in low concentrations is well known. Intensive research is being conducted on the nature of these pollutants, their sources, and their effects. The need for a simple procedure for the determination of them is evident. In order to combat many air pollution problems, the pollutants must be identified and measured. This laboratory has developed a simple method of quantitative removal of volatile contaminants (especially organic vapors) from air, with subsequent determination by conventional analytical methods.

100% adsorption of contaminants may be accomplished by passing the contaminated air stream through a column of activated charcoal. However, any water vapor present is adsorbed from the air along with the contaminants thus increasing the weight and thereby making gravimetric determination impractical. No drying agent for water has been found which will not take up small amounts of contaminants, when both are present in air.

In view of the above difficulties, it was decided to remove both the contaminants and the water vapor from the air stream by condensation at low temperatures with subsequent analysis of the condensate by conventional means such as a chemical procedure, or by infrared spectroscopy. A dry ice and acetone bath is a well known method of conveniently obtaining moderately low temperature and this was found to be suitable for the complete condensation of vapors under consideration. Although liquid air and other coolants will produce much lower temperatures, they have not been found to be necessary to date.

Apparatus and Reagents

50 lb. dry ice.
5 gal. acetone, commercial grade.
Dry ice bath, flow-meter, *etc.* as shown in Fig. 1, 2 and 3.

Procedure

Description of Method

A known amount of the air mixture (in this case 2 *l.*/min. at 760 mm. Hg and 20°C.) as measured by a flowmeter, is passed through the apparatus. Both water and contaminants are condensed out by means of the low temperature dry ice-acetone immersion bath, which maintains a constant temperature of approximately —77°C. The air mixture is first passed through an entrainment trap for removal of any liquid entrained in the air stream. It then passes through 3 traps in series, each immersed in the dry ice-acetone bath which condenses and removes all the water and contaminants. If any contaminant should pass these traps it will be adsorbed by the tube of activated charcoal which is placed at the discharge of the traps. (Since no gain in weight has been detected at the carbon trap, efficient and complete contaminant removal by the first 3 traps is demonstrated).

The contaminants present in the entrainment trap and in the 3 cold traps may be determined by analytical means. This weight of material (added to the weight, if any, of contaminant adsorbed by the carbon) will give the total for a given time and for a given volume of vapor mixture.

Preparation of Apparatus (See Fig. 1)

Place apparatus close to the source of the air stream to be analyzed, and, (if possible) keep the vacuum pump close to the apparatus.

Insert inlet line (IL) into vapor stream, keeping inlet valve (IV) closed.

Connect outlet line (OL) to vacuum pump. Valve (OV) should be closed.

Fill pressure regulators (P_1, P_2, P_3) ¾ full of water.

Note: *The flowmeter (F) is pre-calibrated for a flow of 2 l./min. with a bulb charge of 25 ml. of water which is usually colored by the use of a water soluble dye.*

Clean, dry and weigh entrainment trap (ET) and traps T_1, T_2 and T_3 (see Fig. 2 and 3) using rubber seals on inlet and outlet of each trap while weighing. Assemble these traps on the apparatus and connect inlet line (IL) to inlet side of entrainment trap (ET).

Fill carbon tube (CB) with dry, Type No. KE-1 (8 x 12 mesh, 50 min. activity) coconut charcoal and weigh, using rubber seals on inlet and outlet. Assemble carbon tube on apparatus.

Fill bath 2/3 full with acetone and add crushed dry ice slowly. Violent

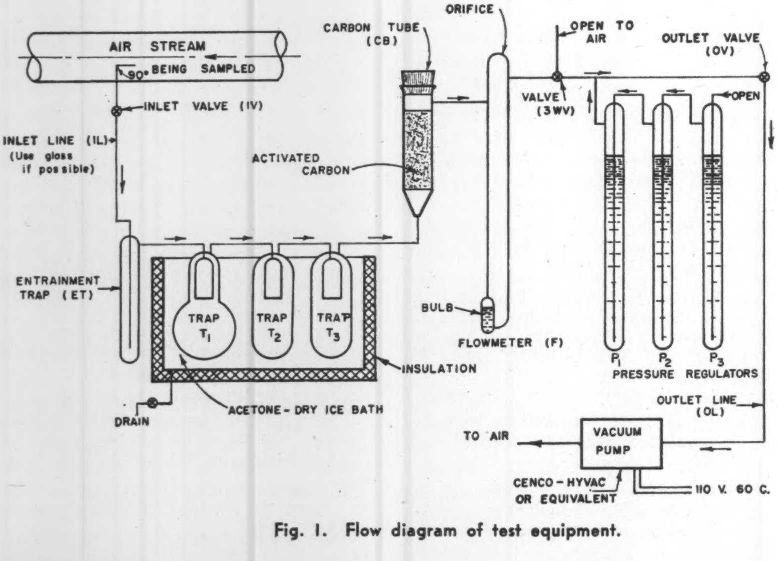

Fig. 1. Flow diagram of test equipment.

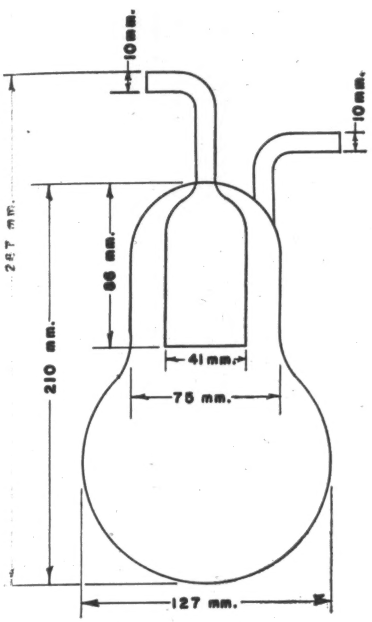

Fig. 2. Trap T_1.

evolution of carbon dioxide gas will take place until the temperature of the bath reaches approximately −77°C. The bath should be kept full of acetone and dry ice at all times and additional dry ice should be added at 30 min. intervals in order to maintain a balance of approximately 50% dry ice and 50% acetone in the bath.

NOTE:

(1) *Do not allow the bath mixture to contact the skin at any time.*

(2) *Fifty pounds of dry ice should be sufficient to operate apparatus for 8 hrs.*

(3) *The dry ice-acetone mixture, after use, should be allowed to come to room temperature before confining in a closed vessel, since the CO_2 dissolved in the acetone can form excessive pressures if confined at elevated temperatures.*

(4) *Since acetone is inflammable, the usual precautions should be observed in order to prevent fires.*

Operation of Apparatus

Check all connections to make sure they are tight.

Start vacuum pump (Cenco-Hyvac, or equivalent) and open inlet valve (IV). By the use of both valve (3WV) and valve (OV) adjust flow at flowmeter to 2 *l.*/ min. at the same time having a steady stream of bubbles passing thru pressure regulators (P_1, P_2, P_3).

Check time to the nearest minute.

The apparatus is now in operation, and can be operated for a suitable period, up to the capacity of the traps (T_1, T_2 and T_3). Depending on the concentration of the contaminant in the air stream being tested, the test period may vary from 30 min. to several days. However, the governing factor will be the amount of contaminant condensed in T_1, T_2 and T_3. It is recommended that at least 10 g. of material be collected, unless micro analytical methods are used.

Check flowmeter at regular intervals and the dry ice-acetone bath at 30 min. intervals.

If the air being sampled contains high concentrations of water vapor, the bell of trap (T_1) may have a tendency to plug with ice (this is shown by a gradual falling off of air flow as indicated by the flowmeter). Gentle tapping of trap (T_1) will usually cause this snow to fall to the bottom of the trap. Another source of plugging due to snow may be at the connections between traps. Any snow forming in these can be seen and quickly eliminated by the application of a few drops of warm acetone to the outside of the connections.

Tests are usually run for 8 hrs. At the end of the test period, close inlet valve (IV) and valve (3WV), shut down the vacuum pump and close outlet valve (OV).

Weigh entrainment trap (ET) and carbon tube (CB) using rubber seals as before. Raise traps (T_1, T_2 and T_3) from bath; install rubber weighing seals, and allow traps to warm to room temperature, at which time they may be weighed. Keep rubber seals on traps after weighing.

Determination of Contaminants

After weighing traps (T_1, T_2 and T_3) pour contents of all 3 traps into 1 stoppered container. Add 10 ml. of distilled water to each trap, weigh again, swirl water in trap and pour contents into container. If certain of the contaminants are volatile at room temperature, the traps should not be disturbed until provisions are made for analyzing the gas phase of their contents.

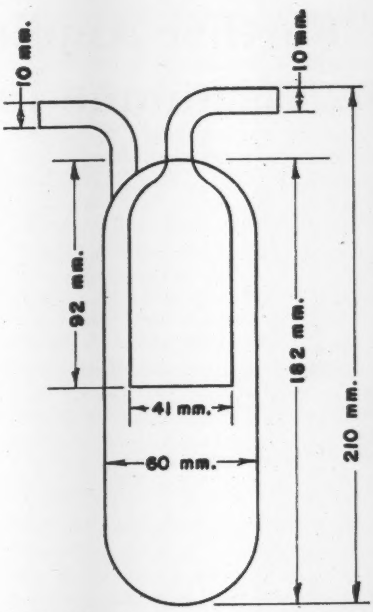

Fig. 3. Trap T_2 and T_3. (Dimensions are approximate.)

The entrainment trap (ET) is treated in the same manner if it has picked up any entrained liquid. However, in the majority of cases no gain in weight will be noted for this trap, in which case it may be disregarded.

The composite sample obtained from traps (T_1, T_2 and T_3) and possibly (ET) can then be analyzed for the particular contaminant or mixture of contaminants being dealt with in the determination.

It would not be practical to list the methods of testing for the various compounds in this report. The methods for determination of most materials are given in detail in the proper analytical literature.

After the determination has been made, the following formula is used to calculate the concentration of vapor in the original mixture:

Calculations

$$\frac{\text{Wt. Contaminant Trapped (G.)}}{2l./\text{min. x Time (Min.)}} = \text{Concentration of Contaminant (G./}l.\text{)}.$$

(To convert from g./*l.* to lb./ft.^{3} multiply by 0.0624).

Discussion

By the use of this method, quantitative removal and subsequent analysis of volatile contaminants in air streams has been demonstrated in numerous tests. The procedure is simple and effective and should prove a valuable analytical method for air pollution studies.

Further Applications of the Limed Filter Paper Technique in Fluorine Air Pollution Studies

DONALD F. ADAMS
Division of Industrial Research
State College of Washington
Pullman, Washington

The exposure of lime-treated filter papers under protection of wooden shelters as an inexpensive and reliable technique to detect atmospheric fluorides and to delineate areas of fluoride pollution was first proposed by Miller, *et al.*(1) These authors found an excellent statistical relationship between the fluoride accumulated by the chemically treated filter papers exposed to the atmosphere for 4 week periods and the forage fluoride levels accumulated for the same interval. This relationship was particularly reliable when the forage fluoride levels found were above 20 ppm. Robinson(2) has recently reported studies concerning the relative effectiveness of fluoride absorption by lime-treated filter papers unprotected by shelters in ambient fluoride-polluted air as compared with similar papers exposed within experimental greenhouses through which the outside air was circulated at a constant flow rate. Unexplained differences in accumulated fluorides were observed under 2 conditions of exposure. Ost(3) suspended unsheltered lime-treated cloths in trees for 5 to 7 months. MacIntire, *et al.*(4) reported the use of Spanish moss *(Tillandsia usneoides)* suspended in trees, both sheltered and unsheltered, as a means of concentrating atmospheric fluorides. Wander and McBride(5) have recently used Spanish moss in their studies of atmospheric pollution in Florida. Compton and Remmert(6) have utilized potted buckwheat and cabbage plants as accumulators of fluorides. In each technique the various authors have determined the fluoride content of the absorbing medium. The varying fluoride levels found have been reported as a measure of the relative intensity of fluoride pollution at the sampling site for the absorbing period.

Methods utilizing plant material of various types have some of the following disadvantages: they require watering and care, a source of supply is not always readily available, they cannot be used in the winter in many areas, they may be injured or destroyed by insects or disease, space and additional manpower are required to plant and care for specimens to the stage of maturity required for exposure, *etc.* Unsheltered absorbers, both plants and chemically treated surfaces, may be subjected to variations such as washing by rain or loss of accumulated fluorides through attrition by winds. Sheltered, nonliving absorbers obviate these disadvantages.

This present communication is a report of (1) comparative fluoride levels accumulated by lime-treated filter papers exposed in duplicate shelters, (2) the statistical relationship at each of 20 exposure sites between the average monthly filter paper fluoride level for the growing season and the total fluoride level accumulated in heterogeneous ground cover vegetation at each site during the growing season, and (3) the reliability of the lime-treated filter paper technique in measuring the relative intensity of fluoric pollution from one year to another.

Materials and Methods

The shelters in which the treated papers were exposed were essentially as recommended by Miller, *et al.*(1) with the exception that plastic clothes pins which supported the treated filter paper at top and bottom were attached to ¾ in. x ¾ in. wooden strips nailed to each end of the shelter rather than suspended from wires. This modification yielded considerable stability to the filter paper racks and permitted greater ease in changing papers at the conclusion of each exposure period. Each box contained 14 filter papers — 7 on each side in 2 parallel lines. The boxes were supported approximately 5½ ft. above the ground, by stakes and were located away from roads or other local sources of dust. Care was taken in the selection of exposure sites to locate the exposure shelters at a distance at least 5-10 times the height of nearby trees or buildings away from these obstructions.

The lime-treated papers were prepared by dipping Whatman No. 1 or 2, 11.0 cm. filter paper in lime water (10 g./*l.* of Fisher low in fluorine lime). This represents a 64% reduction in the lime concentration recommended by Miller *et al.* (1) This change was found desirable since it produced a paper less subject to the flaking off of excess lime. following drying. The wet, impregnated papers were laid in a large Pyrex tray, drained of any excess lime water, and dried in a forced-draft oven at 50-60°C.

Treated and exposed filter papers were changed on the first day of each month unless otherwise stated and the total fluoride found was corrected to the equivalent of a 30 day month. The exposed papers were dried at 50°C. for 24 hr. and weighed. The papers were then placed in inconel crucibles, 0.25 g. of additional lime low in fluorine and water added to produce a slurry. The crucibles and contents were heated to dryness on a hot plate and initial charring of the paper achieved under infrared lamps, care being taken to prevent flaming of the paper. The partially ashed papers were then placed in a muffle furnace at 600°C. for 30 min. Fluorine was determined by distillation of the ash from perchloric acid by a modified AOAC procedure(7) and the distillate titrated by a modified Smith-Gardner-Williams high salt thorium titration.(8) Results were reported as ppm. fluoride in the absorbing medium.*

At the end of the 1954 growing season a sample of ground cover vegetation available at each of 20 exposure

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* The manner in which results are reported has been altered since preparation of this manuscript. Results are currently reported as $\mu g.$ of fluoride/cm.^{2} of exposed surface of the absorbing medium.

TABLE I

Comparison of Fluoride Content of Lime Papers Exposed in Duplicate Exposure Shelters

Number of Exposure Sites	5
Number of Exposure Shelters at Each Site	2
Number of Duplicate Samples	29
Mean Difference Between Duplicate Shelters, %	8.7
Standard Deviation, %	5.2
Range of Differences, %	1.8 - 19.2

sites was obtained for fluorine analysis. Fluorine in the vegetation was determined by slightly modified sodium hydroxide fusion methods of Remmert, *et al.*(9) and Rowley, *et al.* (10) The vegetation distillates were titrated by the same procedure used in the analysis of the exposed filter papers.

Results and Discussion

(1) Comparative fluoride levels in duplicate shelters

Duplicate filter paper shelters were established at 5 locations within an area surrounding a known source of atmospheric fluorides. The shelters were carefully oriented along the same axis and at the same height from the ground at each of the locations. In each instance the axis along which the papers were hung within the shelter was perpendicular to an imaginary line drawn between the source and the shelter site. The exposure period for all samples reported was 1 calendar month. All of the exposed papers from each shelter were treated as a single sample and the average ppm. fluoride accumulated in the treated papers for each exposure shelter compared with its duplicate shelter. Statistical data indicating the reproducibility of results obtained from the duplicate exposure shelters for a 6 months period is shown in Table I. These data show that under similar conditions of exposure only small differences in fluorine content may exist between duplicate shelters.

(2) Curvilinear relationship between average monthly lime paper fluoride levels and fluoride accumulated in herbage during the growing season

Twenty-two exposure sites were located within another area containing known sources of fluoride pollution. Lime papers were exposed and analyzed on a monthly basis throughout the growing season of 1954, May through September. A sample of the available heterogeneous herbage available at each of the exposure sites was obtained on October 1, 1954, and the fluoride content determined. Late summer grass fires prevented obtaining vegetation samples at 2 of the exposure sites.

Linear and curvilinear regressions were calculated for the relationship between the average monthly lime paper fluoride levels and the total fluoride accumulated by the vegetation throughout the entire growing season for the 20 exposure sites where complete data was available. The curvilinear relationship showed a significant improvement in relationship between the variables. These results are summarized in Tables II and III and are graphically presented in Fig. 1.

The correlation between the fluoride in the lime papers and the ground cover vegetation for a wide range of fluoride exposure levels (3.6-139.6 ppm. F. in lime paper and 13-163 ppm. F. in vegetation) is quite high, as indicated by the *r* value of + 0.922. This *r* value is well in excess of that required for confidence at the 1% probability level. From these data, it is apparent that even the fluoride content of heterogeneous herbage accumulated throughout the entire growing season can be predicted with a reasonable degree of accuracy from the average monthly fluoride content of lime papers exposed during the growing season.

(3) Lime paper technique in measuring relative fluoride pollution levels from one year to another

Lime filter papers were again exposed at the same 22 locations men-

TABLE II

Curvilinear Correlation Between Fluorine in Lime Papers and in Ground Cover Vegetation

Exposure Site No.	X Average Monthly Lime Paper Fluoride Level (ppm. F^-)	Y Accumulated Fluoride Level in Vegetation (ppm. F^-)	Y Predicted Fluoride Level in Vegetation (ppm. F^-)
1	7.0	21	30
2	21.8	*	*
3	51.8	68	104
4	75.4	*	*
5	139.6	163	162
6	14.8	38	45
7	13.2	51	42
8	79.4	141	135
9	10.2	24	36
10	6.8	16	30
11	7.2	19	30
12	8.4	30	33
13	4.2	37	24
14	3.6	13	23
15	10.8	37	37
16	10.0	49	36
17	8.2	26	32
18	10.6	25	37
19	26.4	109	66
20	29.2	66	71
21	11.0	73	38
22	78.0	138	133

*Samples unobtainable due to grass fire.

N	20
r	+ 0.922
Standard error of estimate	$y = \pm 18.1$ ppm. F^-
Curvilinear regression equation	$Y = 15.731545 + 2.087458X - 0.007404X^2$

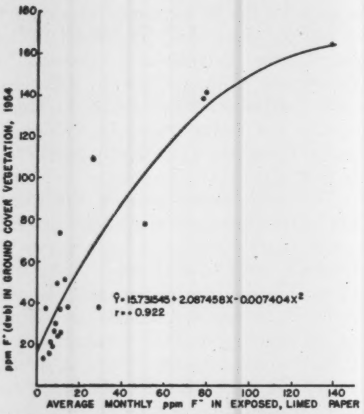

Fig. 1. Curvilinear relationship between fluoride leveles in lined filter paper and ground cover vegetation at 20 exposure sites in 1954.

$Y = 15.731545 + 2.087458 \times -0.007404 \times^2$
$r = + 0.922$

TABLE III

Comparison of Linear and Curvilinear Correlations Between Fluorine in Lime Papers and in Ground Cover Vegetation

	d.f.	S.S.	M.S.
Total	19	39436	
Linear Regression	1	31615.58	31615.58**
Quadratic Regression	1	1903.72	1903.72*
Residual	17	5916.70	348.04

*$P < 0.05$

r (linear correlation)	+0.887
r (curvilinear correlation)	+0.922

tioned above during the 1955 growing season. The first exposure period commenced on May 15, and continued until June 15. Three 15 day exposure periods followed. Exposures for August and September were made on a monthly basis. All lime paper fluoride levels were converted to an equivalent 30 day exposure basis. Exposure sites 14 and 17 were chosen by reason of their elevation and location as being representative of background fluoride levels which might accumulate on the limed paper from fluoride-containing dust normal to the region. The average fluoride level found in the limed papers exposed during 1955 was 1.6 ppm. This average background fluoride level was subtracted from all of the fluoride levels found at the other sampling sites, to give an indication of the proportion of the accumulated fluorides which might be due to atmospheric pollution in contrast to the normal fluoride content of the air. Table IV records the comparison of the average monthly fluoride level for each of the exposure sites in 1954 with similar levels for 1955 and the corrected levels for each of these sites. The data from the 22 exposure sites indicates that an average reduction of 65.2% in fluoride pollution was experienced throughout the survey area. A consideration of the average lime

TABLE IV

Comparison of Average Fluorine in Lime Papers in 1954 and 1955.

Exposure Site No.	Approximate Distance From Major Source (miles)	1954 Average Monthly Lime Paper Fluoride Level (ppm. F^-)	1954 Average Monthly Lime Paper Fluoride Level Corrected For Background (ppm. F^-)	1955 Average Monthly Lime Paper Fluoride Level (ppm. F^-)	1955 Average Monthly Lime Paper Fluoride Level Corrected For Background (ppm. F^-)	% Decrease 1954-1955
1	14.5	7.0	5.4	4.9	3.3	37.7
2	8	21.8	20.2	9.8	8.2	59.4
3*	5	51.8	50.2	20.0	18.4	63.3
4*	5.5	75.4	73.8	22.7	21.1	71.4
5*	4.5	139.6	138.0	38.0	36.4	73.6
6	16	14.8	13.2	6.7	5.1	61.4
7	13	13.2	11.6	4.4	2.8	75.9
8*	8	79.4	77.8	20.6	19.0	75.6
9	22.5	10.2	8.6	4.6	3.0	65.1
10	25.5	6.8	5.2	5.1	3.5	32.7
11	30	7.2	5.6	3.8	2.2	60.7
12	24	8.4	6.8	4.2	2.6	61.8
13	26	4.2	2.6	3.6	2.0	23.1
14	29	3.6	2.0	1.7	0.1	95.0
15	21	10.8	9.2	3.7	2.1	77.2
16	20.5	10.0	8.4	4.7	3.1	63.1
17	19	8.2	6.6	1.6	0	100.0
18	16.5	10.6	9.0	4.4	2.8	68.9
19	13.5	26.4	24.8	10.7	9.1	63.3
20	10.5	29.2	27.6	10.9	9.3	66.3
21	17.5	11.0	9.4	4.6	3.0	68.1
22*	7	78.0	76.4	23.6	22.0	71.2
						65.2
						71.0

Average % decrease in lime paper fluoride level at 22 sites.
*Average % decrease in lime paper fluoride level at the 5 sites within a similar topographical area as the alleged source.

paper fluoride levels at the 5 exposure sites located north and east of the major alleged fluoride source and within the same topographical area indicates a 71.0% abatement in the fluoride pollution level at these sampling sites from 1954 to 1955.

Wind data obtained from the nearest U. S. Weather Bureau station subjected to similar macrometeorological influences are summarized in Table V. It will be noted that winds from W to ESE, which would influence the 5 selected sites, comprised 66.7% of the winds in 1954 and 66.0% in 1955. It is apparent from this consideration that the observed diminution in fluoride pollution reflected by the comparative lime paper fluorine levels was primarily due to a reduction in the quantity of emission at the alleged source rather than to any gross variations in the wind pattern.

Data compiled by engineers at the major source of fluoride emission indicate that the installation of air cleaning equipment between 1954 and 1955 effected a 78.1% reduction in the atmospheric fluoride losses from their operation(11) The observed difference between the 78.1% claimed reduction in fluoride emission and the 71.0% reduction noted from the lime paper survey could well be accounted for by an increase in emission rate from a small, secondary source of fluoride pollution located approximately 10 miles south of the major source. The rate of emission and the percentage increase of emission from this secondary source between 1954 and 1955 are unknown to the author. Consideration of these facts and the average reduction of fluoride between 1954 and 1955 at the 5 lime paper exposure sites located within the area of greatest fluoride pollution quantitatively substantiates the reliability of the lime paper technique in measuring the relative intensity of fluoride pollution from one year to another within a given area.

TABLE V

Comparison of Hourly Wind Percent Frequency Distribution For May Through September, 1954 and 1955

Direction	1954	1954 Subtotal	1955	1955 Subtotal
W	3.0%	66.7%	2.0%	66.0%
WSW	0.8		1.0	
SW	2.4		2.6	
SSW	2.1		3.7	
S	15.0		13.6	
SSE	19.8		22.3	
SE	19.0		17.5	
ESE	4.6		3.3	
E	1.8	31.8%	1.8	29.9%
ENE	0.5		0.9	
NE	2.9		2.7	
NNE	3.1		3.3	
N	8.0		4.9	
NNW	5.6		7.0	
NW	7.0		7.2	
WNW	2.9		2.1	
Calm	1.5		4.1	

In any given instance, however, it would be necessary to examine and compare the weather patterns for the exposure periods under consideration. Furthermore, it is recommended that a reasonable number of exposure sites be considered in making such a survey. Examination of the data obtained also indicates a more reliable estimate of relative conditions may be obtained from a consideration of exposure sites located near the source of pollution rather than those located 20-30 miles distant.

Acknowledgement

The author is indebted to the Wasatch County Fluorine Committee for financial support of a portion of the work reported, to J. G. Darroch for assistance in statistical analysis and to R. K. Koppe and student assistants for chemical analysis of samples for fluoride content.

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Emission of Fluorides From Industrial Processes --A Review*

KONRAD T. SEMRAU
Stanford Research Institute
Menlo Park, California

In recent years there have been an increasing number of reports of injury to livestock or vegetation due to atmospheric pollution by fluorides. The importance of fluorine as an atmospheric pollutant was emphasized by a number of investigators at the U. S. Technical Conference on Air Pollution in 1950(65). The increase of pollution by fluorine has been associated with the growth of certain industries, and has become more marked as industrial plants have moved into areas which were previously agricultural.

Fluorine occurs in small quantities in plant and animal matter (34), in the former by uptake from the soil and in the latter by intake of food and water. In animals the fluorine retained is concentrated principally in the bones and teeth. Within certain limits the presence of fluorine is beneficial, reducing the incidence of dental caries. In excessive quantities, however, fluorine may produce in animals a chronic poisoning which is termed *fluorosis*(92,104). However, Schmidt and Rand(104) point out that cattle have a tolerance for fluorine above the amount normally and naturally absorbed, and that above-normal absorption does not necessarily produce injury.

Effects of Atmospheric Fluorine Compounds

Plants show a wide range of susceptibility to injury from gaseous fluorine compounds(115). A factor of great importance is that forage may absorb sufficient fluorine to produce injury to livestock feeding upon it without showing any damage to the foliage itself(115). As a result, atmospheric pollution by fluorides has in a number of cases resulted in secondary damage to cattle without producing any important damage to vegetation.

In some industries that employ fluorine compounds there is a possibility of acute fluorine poisoning, and in some cases concentrations of fluorides in plant atmospheres have been sufficiently high to be at least a potential industrial hygiene problem (30,36,101,114,127). The accepted threshold limit value for human exposure to hydrogen fluoride is 3 ppm. parts of air(27). Atmospheric pollution by fluorides involves concentrations far below the threshold limit, and there has been no demonstrated case of chronic fluorosis, much less of acute poisoning, resulting from inhalation of air containing these low concentrations of fluorine compounds. Although it has been suggested that fluorine compounds may have been prime agents in the air pollution disasters in the Meuse Valley and at Donora, no evidence has been presented to demonstrate that this was the case(27,100,105). Where fluorosis in livestock has occurred, it has resulted from the eating of contaminated forage.

Atmospheric pollution by fluorides has usually involved both gaseous compounds and dusts or fumes. The gaseous compounds have usually been hydrogen fluoride, HF, or silicon tetrafluoride, SiF_4; their relative toxicities to plants have not been determined(115). Little information is available upon the effects of particulate fluorides which settle upon leaves; it appears that any absorption by the leaf should depend upon the solubility of the fluoride. However, even relatively insoluble fluorides present on plants and ingested by livestock may produce fluorosis (61,92). Endemic fluorosis has appeared in areas where forage is contaminated by natural dusts having high fluorine contents(61,104). Development of fluorosis in cattle is, however, related in part to the solubility of the fluoride(92), and fluorides in dusts from industrial sources may be more soluble than those in natural dusts(96). The relative importance of gaseous and particulate fluorides in development of fluorosis has been a subject of dispute(6,26,61,128).

Sources of Atmospheric Fluorine Compounds

Fluorine contaminants may be emitted to the atmosphere by a wide variety of industrial processes in which fluorine compounds are manufactured, utilized as catalysts or fluxes, or are present as impurities in the process materials. In some cases, the possibility of contamination is obvious, and control measures are generally provided as a matter of course. These include manufacture of HF (130), use of HF as an alkylation catalyst in the manufacture of motor fuels(27), and use of elemental fluorine(60,118). However, some of the most serious cases of pollution have arisen from processes in which fluorine compounds are used as fluxes or are present as impurities. In some instances, the fluorine has been present in the process material in a concentration so low that its presence was not considered to constitute a potential problem, or perhaps was not even recognized.

Fluorosis in cattle, or damage to vegetation, has occurred primarily in the vicinity of plants manufacturing phosphate fertilizers(61,98), aluminum (1,61,98), brick (6,100,101), enamel frit (6,15,16,41-46), and iron and steel(6,40-46). MacIntire(69) considers that the most important sources are probably the manufacture of phosphate fertilizers, aluminum, and steel. Fluorosis in cattle resulting from emissions from a superphosphate plant was recognized in Italy as early as 1912(61,100, 101). Some of the older European literature indicates that it may have existed much earlier around the smelters in Freiberg, Germany(27,100). Existence of the disease in the United States has been recognized only comparatively recently(52).

Although the industries listed above are those that have been recognized as producing damage in certain instances, numerous other industries may actually or potentially emit fluorine compounds to some degree in processing minerals and ores. Fluorine is present in relatively large quantities throughout the earth's crust, recent estimates placing it as the thirteenth in order of abundance among the elements(58). Earlier estimates were considerably lower(63). Fluorine is widely distributed, frequently in relatively small concentrations. Samples of top soils in the United States have been found to contain from 20-1640 ppm. of fluorine (61). The most common fluorine minerals are fluorite, or fluorspar, CaF_2, and fluorapatite, $Ca_{10}(PO_4)_6F_2$, the principal constituent of phosphate rock. Simple fluorine-containing minerals other than CaF_2 are comparatively rare, but a great many complex minerals containing fluorine are known(34,58). The latter include cryolite and complex silicates such as topaz and some micas and hornblendes.

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* Presented at the 130th Meeting of the American Chemical Society held at Atlantic City, N. J., September 1956.

Fluorite occurs in association with numerous other minerals, such as limestone and calcite(34,58). It is a common gangue mineral of ore deposits, and is frequently associated with pyrite, chalcopyrite, sphalerite, and galena(58,80). Sulfide ores containing up to 0.35% of fluorine have been reported(35). Certain iron ores have also been reported to contain fluorine, probably as fluorapatite (6,31). Clays have been reported to have fluorine contents in the range 450-1600 ppm.(6,101), and coal usually contains small amounts of fluorine (8,19,22).

Mechanisms of Liberation of Fluorine Compounds

Fluorine may be emitted from processes either as gaseous compounds or as particulate matter consisting of either solid fumes or mechanically-entrained dust, or of mists. The mechanically-entrained dust may be expected in general to be of relatively large particle size and of a composition similar to that of the original process material. However, fumes formed by volatilization of metal fluorides may be of fine particle size and have a higher fluorine content than the original process material. Mists may be formed by solution of gaseous fluorides in fine water droplets.

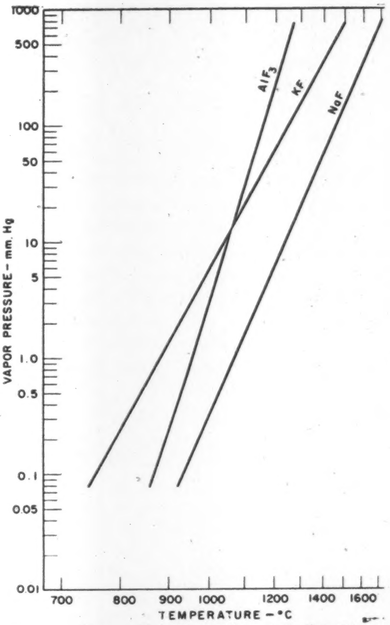

Fig. 1. Vapor Pressures of Metal Fluorides.

Gaseous fluorides formed in various processes are generally SiF_4 or HF, although it has been suggested that boron trifluoride, BF_3, may be formed in some cases. The activity of elemental fluorine is so great that there appears little likelihood that it is ever formed, or has more than a transitory existence, in any ordinary chemical or metallurgical process. Therefore, as used in this paper, *fluorine* is considered to denote only fluorine in the combined, rather than the elemental, state. Although many volatile fluorides are known(108), most are very reactive or else require for their formation conditions which do not exist in the usual chemical processes, and hence are unlikely to appear in effluents.

TABLE I

Melting and Boiling Points of Fluorides

Compound	M. P. (°C.)	B. P. (°C.)	Reference
CaF_2	1418	2500	(34)
NaF	980-1040	1705	(34)
KF	850	1500-1505	(34)
AlF_3	1040		(34)
	1040	1537	(112)
		Subl. 1260	(58)
		Subl. 1291	(58)
	> 1272	Subl. 1272	(94)

Among the stable metal fluorides there are several which at elevated temperatures have vapor pressures high enough to permit appreciable formation of fumes. These are the fluorides of the alkali metals and of aluminum(94). In Table I are given the melting and boiling points of the fluorides of calcium, sodium, potassium, and aluminum; some of the values are not well established. AlF_3 has been reported to melt at 1040°C. (34); however, other information(58, 94) shows it to sublime in the range 1260°-1291°C. In Fig. 1 are presented the vapor pressure curves for NaF, KF, and AlF_3. The curves for NaF and KF were plotted from the data reported by Stull(112) and Brewer(94), which are in close agreement, whereas that for AlF_3 was prepared from the data of Brewer, which were considered to be the most reliable.

From these data it can be seen that no significant quantities of CaF_2 are likely to be volatilized in even relatively high temperature processes, but that fumes of NaF, KF, and AlF_3, may be formed if these compounds are initially present in a process material or are formed through reactions of less volatile fluorides, such as CaF_2, which may be present in process materials.

Fluorides may be volatilized through a number of reactions; the more important type reactions are presented in Table II. CaF_2 is assumed in appropriate cases to be the non-volatile starting material, as it probably is in many instances.

SiF_4 is known to be formed during treatment of phosphate rock with sulfuric (or phosphoric) acid to form superphosphate(77,106,107,120,126). The formation of the SiF_4 probably results from a series of steps illustrated by Reactions 1 to 4(77,126). The reaction of the sulfuric acid with the calcium fluoride (or, actually, fluorapatite) produces HF which subsequently reacts with silica present in the phosphate rock according to Reactions 2 or 3.

Fluosilicic acid, H_2SiF_6, does not exist as such in the vapor state(108);

the vapor phase consists of a mixture of SiF_4 and HF. In a hot, acid medium, H_2SiF_6 decomposes according to Reaction 4.

SiF_4 may be formed at elevated temperatures by a number of reactions. Fluosilicates are decomposed (108) into the normal fluoride and SiF_4, as illustrated by Reaction 5. The dissociation of Na_2SiF_6 becomes appreciable at about 327°C. Reactions 6 to 8 have been frequently reported, but as is shown below, there is little evidence that they are of importance.

SiF_4 undergoes reactions with water in both the liquid and the gas phases. If the liquid phase, H_2SiF_6 is formed according to Reaction 9. Reaction 9 expresses only the net reaction; apparently the actual process consists of a series of steps which are discussed by Simons(108) and Whynes (126). The gas phase reaction of water vapor with SiF_4 (Reaction 10) has been studied by Lenfesty, *et al*(64), who found that the equilibrium favored formation of SiF_4 at low temperatures and of HF at high temperatures.

BF_3 may be formed(108) by Reaction 11 or a similar reaction between the metal fluoride and boric oxide. This method was originally used to prepare BF_3. BF_3 undergoes hydrolysis even at ordinary temperatures (58,108).

HF may be formed(28) by the reaction of water vapor with metal fluorides at high temperatures, as illustrated by Reactions 12 to 14. This type of reaction has been used for fluoride analysis(122) and for defluorination of phosphate rock on a commercial scale(14). These hydrolysis reactions may be promoted by the presence of acidic oxides, as in Reactions 15 and 16. The hydrolysis of cryolite(58) by water vapor (Reaction 17) is similar.

Volatile metal fluorides may be formed by reaction of their oxides, carbonates, or silicates with calcium fluoride (Reactions 18 to 21). In minerals the alkali metals generally occur as more or less complex silicates. Reactions 18 and 19 have been demonstrated(70,103), and Reaction 21 is reported to take place at red heat (34). Reaction 20 takes place during the manufacture of Rhenania phosphate(121).

Thermodynamics of Fluorine Reactions

As noted above, a number of the reactions listed in Table II are known to take place, at least between the pure components and under laboratory conditions. However, not all may be of importance. In particular, although formation of SiF_4 in high temperature processes according to Reactions 6, 7 or 8 has frequently been reported, there is little evidence that it was actually significant, or that the observed volatilization of fluorine was not the result of other types of reactions. Therefore, an attempt has been made to determine what the potentialities of some high temperature reactions are by calculation of their free energies and of certain equilibria.

Free Energies

From data available in the literature, the standard free energies of Reactions 7, 8, 12, 13, 14, 18, and 19 have been calculated and plotted as functions of temperature (Fig. 2 and 3). The free energies are given as kilocalories/gram-mole of fluorine. The data were obtained from the free energy-temperature diagrams of Kellogg(57) and Osborn(89). Kellogg gives free energies of formation of fluorides, while Osborn presents those for oxides and silicates.

The accuracy of some of the free energies of formation is limited (57,89). Kellogg indicates probable errors of 1-3 kilocalories/mole/of fluorine in the values for fluorides in the range from 1000°C. up. Osborn indicates an uncertainty of ± 5 kilocalories/gram mole in values for most of the oxides and silicates, with uncertainties greater than ±5 kilocalories in others. Because of difficulties in reading the diagrams given by Kellogg and Osborn, the free energies of formation were read only to 1 kilocalorie. Consequently, the uncertainty in the values given in Fig. 2 and 3 is probably not less than ±5 kilocalories. Data for the oxides and silicates of sodium and potassium were lacking for much of the range of interest at the higher temperatures; the broken lines are extrapolations indicating the apparent trends.

Murphy and Rubin(81) have carried out more precise calculations of $\triangle F°$ for Reaction 12 at 298°, 500°, 1000°, and 1500°K. Their values for 298° and 500° are in very close agreement with those taken from Fig. 2, but those for 1000° and 1500° are about 4 kilocalories lower, which is within the range of uncertainty.

TABLE II

Reactions of Fluorides

	Formation of Silicon Tetrafluoride In An Acid Medium
1.	$CaF_2 + H_2SO_4 = CaSO_4 + 2\ HF$
2.	$4\ HF + SiO_2 = SiF_4 + 2\ H_2O$
3.	$6\ HF + SiO_2 = H_2SiF_6 + 2\ H_2O$
4.	$H_2SiF_6 = SiF_4 + 2\ HF$
	Formation of Silicon Tetrafluoride in Thermal Processes
5.	$Na_2SiF_6 = 2\ NaF + SiF_4$
6.	$CaF_2 + 1/2\ SiO_2 = CaO + 1/2\ SiF_4$
7.	$CaF_2 + 3/2\ SiO_2 = CaSiO_3 + 1/2\ SiF_4$
8.	$CaF_2 + 1/2\ CaSiO_3 = 3/2\ CaO + 1/2\ SiF_4$
	Reactions of Silicon Tetrafluoride With Water
9.	$3\ SiF_4 + 2\ H_2O = 2\ H_2SiF_6 + SiO_2$
10.	$SiF_4\ (g) + 2\ H_2O\ (g) = SiO_2\ (s) + 4\ HF\ (g)$
	Formation of Boron Trifluoride
11.	$6\ CaF_2 + 5\ B_2O_3 = 4\ BF_3 + 3\ Ca_2\ B_2\ O_5$
	Formation of Hydrogen Fluoride By Hydrolysis
12.	$CaF_2 + H_2O = CaO + 2\ HF$
13.	$2\ NaF + H_2O = Na_2O + 2\ HF$
14.	$2/3\ AlF_3 + H_2O = 1/3\ Al_2O_3 + 2\ HF$
15.	$CaF_2 + H_2O + SiO_2 = CaSiO_3 + 2\ HF$
16.	$CaF_2 + H_2O + Al_2O_3 = Ca\ (AlO_2)_2 + 2\ HF$
17.	$Na_3AlF_6 + 2\ H_2O = Na\ AlO_2 + 2\ NaF + 4\ HF$
	Formation of Volatile Metal Fluorides
18.	$CaF_2 + Na_2SiO_3 = CaSiO_3 + 2\ NaF$
19.	$CaF_2 + K_2SiO_3 = CaSiO_3 + 2\ KF$
20.	$CaF_2 + Na_2\ CO_3 + SiO_2 = CaSiO_3 + CO_2 + 2\ NaF$
21.	$CaF_2 + 4/3\ Al_2O_3 = Ca(AlO_2)_2 + 2/3\ AlF_3$

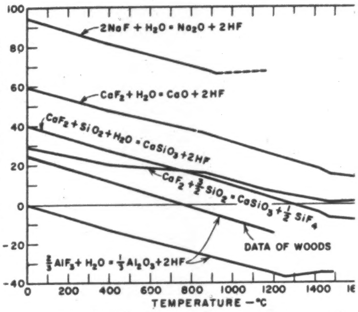

Fig. 2. Standard free energies of fluoride reactions.

Woods[128a] has also computed △F° values for Reaction 14, using the value of heat of formation of AlF_3 at 298°K given by Gross, *et al* [46a]. These values, which have been plotted in Figure 2, indicate greater resistance of AlF_3 to hydrolysis than do those computed from the data of Kellogg. They also appear to be much more nearly in agreement with the observed stability of AlF_3 toward hydrolysis at ordinary temperatures.

From Fig. 2 and 3 it is obvious that AlF_3, although stable at ordinary temperatures, should be susceptible to hydrolysis at high temperatures, as reported by Kirk and Othmer[58]. NaF should, on the contrary, be relatively resistant to hydrolysis, as reported by Warf, *et al* [123], while CaF_2 occupies an intermediate position. The great effect of silica in reducing the free energy of the hydrolysis of CaF_2 is noteworthy. The effect of additives in both shifting the equilibrium and accelerating the rate of such hydrolysis reactions has been discussed by Warf, *et al*[123] and Briner[12]. Aluminum oxide was found to promote the hydrolysis of both calcium and sodium fluorides [123].

The reaction of a number of metal fluorides with water vapor at high temperatures was studied by Domange [28], who determined the equilibria experimentally. He found that the susceptibility to hydrolysis decreased in the following order: CuF_2, FeF_3, AgF, FeF_2, CrF_3, ZnF_2, NiF_2, CoF_2, CdF_3, PbF_2, MnF_2, MgF_2, CaF_2, BaF_2. The degree of hydrolysis increased with increase in the temperature.

Warf, *et al*[123] applied hydrolysis reactions at elevated temperatures to the analysis of halides. They adopted the term *pyrohydrolysis* to describe such reactions, and the term has also been adopted in this paper.

Reaction Equilibria

From the △F° values of Fig. 2 and 3, the equilibrium constant (K_p) for a given reaction may be calculated from the relation

$$\triangle F^\circ = -2.303\ RT \log_{10} K_p$$

The K_p value may then be used to calculate concentrations of a volatile fluoride formed under various conditions.

Equilibrium constants for Reactions 7, 8, 12, and 15 at a number of temperatures are presented in Table III. Values of K_p for Reaction 10, computed from the experimental data of Lenfesty, et al[64] are also presented. The experimental values of K_p for Reaction 12 determined by Domange[28] have been included for comparison; these are much larger than those computed from the free energies of Fig. 2. However, Brewer, *et al*[94] evaluated Domange's data and concluded that they lead to a value for the heat of formation of calcium fluoride at 298°K which is about 6 kilocalories too small.

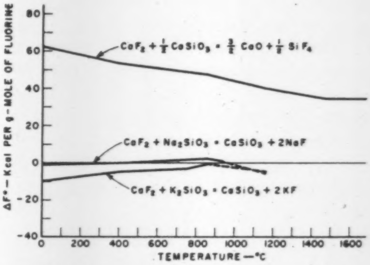

Fig. 3. Standard free energies of fluoride reactions.

In order to calculate equilibrium concentrations of fluorides for the given reactions it is necessary to make certain assumptions as approximations. The actual activities of the components in these systems at high temperatures are not known. In the illustrations given below, it is assumed that solid phases are insoluble in one another, that in liquid systems the activities of components are equal to their mole fractions, and that the activities of gases are equal to their

TABLE III

Equilibrium Constants For Fluoride Reactions
K_p (Equilibrium Constant)

Temperature (°C)	Reaction (10)*	Reaction (7)	Reaction (8)	Reaction (12)	Reaction (12)**	Reaction (15)
100	2.71×10^{-12}					
200	1.13×10^{-8}					
400	1.16×10^{-4}					
600	1.72×10^{-2}	3.1×10^{-5}		3.1×10^{-11}		5.5×10^{-6}
700		1.5×10^{-4}		1.1×10^{-9}		5.4×10^{-5}
800	0.396	5.5×10^{-4}		1.8×10^{-8}		5.5×10^{-4}
900		1.6×10^{-3}		3.0×10^{-7}	2.51×10^{-5}	3.8×10^{-3}
1000	3.41	8.7×10^{-3}		4.8×10^{-6}	1.33×10^{-4}	2.8×10^{-2}
1100		3.7×10^{-2}		3.5×10^{-5}	5.40×10^{-4}	0.11
1200	16.4	0.13	1.6×10^{-6}	2.0×10^{-4}		0.36
1300						1.0
1400	54.0	0.55	2.7×10^{-5}	3.3×10^{-3}		2.5
1600	138	0.76	1.1×10^{-4}	2.3×10^{-2}		8.6

Computed from free energy data from Figs. 2 and 3 except as noted.

Notes: *From data of Lenfesty, *et al* (64)

**From data of Domange (28)

partial pressures. The total pressure is assumed to be 1 atm.

The following illustrations are intended to represent, in very simplified form, cases similar to those which may be encountered in practice. These show that formation of SiF_4 should be relatively unimportant compared to formation of HF by pyrohydrolysis.

If there is no liquid phase at 600°C., then for Reaction 7:

$$K_p = P^{1/2}_{SiF_4}$$

The corresponding concentration of SiF_4 is only 1 part per billion by volume.

At the same temperature (600°C.) for both Reactions 12 and 15:

$$K_p = \frac{P^2_{HF}}{P_{H_2O}}$$

If the water vapor concentration in the gas phase is 10 percent by volume (the usual order of magnitude in combustion waste gases), then the corresponding concentration of HF is 2 ppm. by volume for Reaction 12 and 740 ppm. for Reaction 15.

At higher temperatures, the concentrations of both SiF_4 and HF would increase. However, the assumption of unity activity for all solid components can hardly be justified in general.

At 1600°C., a lime-silica-fluorite system may be assumed to be entirely liquid. If one assumes a system of the composition

Component	*Mole Fraction*
CaO	0.20
$CaSiO_3$	0.75
CaF_2	0.05

then, for Reaction 8:

$$K_p = \frac{[CaO]^{\frac{3}{2}} P^{1/2}_{SiF_4}}{[CaSiO_3]^{1/2} \, [CaF_2]}$$

The corresponding concentration of SiF_4 is only 3 ppb.

For Reaction 12:

$$K_p = \frac{[CaO] \, P^2_{HF}}{[CaF_2] \, P_{H_2O}}$$

and for a water vapor concentration of 10%, the corresponding concentration of HF is 2.4%.

The assumed liquid phase has a lime-silica ratio similar to that of phosphate electric furnace slag (18), and the CaF_2 content is probably of the order of magnitude occurring there.

If, now, one assumes (again at 1600°C.) a siliceous melt of composition

Component	*Mole Fraction*
SiO_2	0.20
$CaSiO_3$	0.75
CaF_2	0.05

then, for Reaction 7:

$$K_p = \frac{[CaSiO_3] \, P^{1/2}_{SiF_4}}{[CaF_2] \quad [SiO_2]^{\frac{3}{2}}}$$

and the equilibrium concentration of SiF_4 is 21 ppm.

On the other hand, for Reaction 15:

TABLE IV

Fluoride Concentrations In Process Waste Gases

Process	Process Equipment	Form of Fluorine	Fluorine Concentration (gr. F./ft.^{3}) *	Reference
Nodulizing phosphate rock	Rotary kiln	HF NaF	0.706 0.029	(90)
Nodulizing phosphate rock	Rotary kiln	HF	1.05	(50)
Defluorinating phosphate rock (molten)	Shaft furnace	HF	1.4-2.8	(50)
Fusing phosphate rock	—	HF	1.6-3.6	(82)
Manufacture of superphosphate	Dens	SiF_4	1-23	(46)
Manufacture of superphosphate	Continuous dens Batch dens	SiF_4	2.1-14.2 16.0-45.3	(107)
Manufacture of enamel frit	Melting furnace	Gaseous and particulate	1.4-1.9	(15)
Manufacture of enamel frit	Melting furnace	—	0.1	(43)
Enamel works	—	—	0.3-0.4	(45)
Brick works	Kiln	—	0.26	(101)
Steel manufacture	Open hearth furnace	HF	0.1	(40)
Steel manufacture	Open hearth furnace	—	0.2	(45)
Steel manufacture	Open hearth furnace	Particulate	0.008	(105)
Aluminum alloy processing	Open hearth furnace	Gaseous	0.005-0.012	(3)
Aluminum melting	Open hearth reverberatory furnace	Particulate	0.11-0.80	(3)

*Where data are available, concentrations have been referred to 60°F. and 1 atm.

$$K_p = \frac{[CaSiO_3]\ P^2_{HF}}{[SiO_2]\ [CaF_2]\ P_{H_2O}}$$

and for a water vapor concentration of 10%, the equilibrium concentration of HF is 10.7%.

In addition, the equilibrium of Reaction 10 must be considered. If SiF_4 is assumed to be present initially at a concentration of 100 ppm, in a gas stream of a total pressure of 1 atm. and containing 10% water vapor, then the SiF_4 should at equilibrium be hydrolyzed to the extent of about 10% at 100°C. and about 63% at 200°C., and over 99.5% at 400°C. Therefore, no significant amount of SiF_4 should exist as such in moist, high temperature furnace gases.

Formation of Gaseous Fluorides

While the foregoing equilibrium calculations greatly oversimplify the actual situation, they do indicate that formation of SiF_4 according to Reactions 6, 7, or 8 should not be a major mechanism of liberation of fluorine in most industrial processes. In a system containing high concentrations of both CaF_2 and SiO_2, Reaction 7 might be of greater importance, but in most actual cases the concentration of fluorine is low.

The calculated equilibrium concentrations of SiF_4 are lower than many fluorine concentrations actually found in stack gases from high temperature processes (Table IV). The equilibrium concentrations of HF are much higher than those actually encountered in most cases, so that pyrohydrolysis is probably limited in most cases by reaction kinetics and mass transfer rates rather than by equilibria.

Rates of pyrohydrolysis are known qualitatively to be fairly rapid(14). However, nothing appears to be known regarding the kinetics of formation of SiF_4 by Reactions 6, 7, or 8; reaction rates as well as equilibria may be unfavorable. Since solid-solid reactions would be involved, reaction rates would probably be low at temperatures below the fusion point.

It appears that many reports of emission of SiF_4 from high temperature processes have been based on surmise or on erroneous interpretation of observations. Stack gases from these processes usually contain siliceous dusts as well as both particulate and gaseous fluorides and it is difficult to determine with certainty what the original compounds of fluorine sampled actually were. TVA investigators reported that substantially all of the fluorine emitted from phosphate rock nodulizing kilns, fused tricalcium phosphate furnaces, and calcium metaphosphate furnaces is in the form of HF (50). This conclusion was based upon material balances made on absorption towers(47). The silica found could be accounted for by that in the dust in the stack gases.

Similar conclusions may apply to formation of BF_3. Formation of BF_3 according to Reaction 11 should be possible in processes such as glass manufacture in which boron compounds as well as fluorides are employed. However, the BF_3 would probably be hydrolyzed in the hot, moist stack gases and therefore not be detectable as such.

While most of the data on pyrohydrolysis deal with treatment of phosphate rock, results of some laboratory investigations of other systems support the conclusions reached above. McCaughey, Kautz, and Wells(67) suggested that SiF_4 was formed during preparation of cuspidine, $Ca_4Si_2O_7F_2$, by fusion of fluorite and quartz in a muffle furnace. Silica was lost, and the crucibles used in melting were surrounded by masses of fibrous silica that the investigators believed to be produced by reaction of SiF_4 with water vapor present in the products of combustion. However, silica itself may volatilize at high temperatures, and other investigators have reported such silica deposits to be formed by volatilization from melts(31). The observed loss of fluorine might have resulted from direct hydrolysis of the fluorite by the water vapor in the combustion gases.

Similar studies were made by Nagai and his associates(84,85,86) of the effects of CaF_2 on the thermal synthesis of calcium silicates from mixtures of $CaCO_3$ and SiO_2 and of CaO and SiO_2. They reported(85) that most of the CaF_2 remained in the product when the temperature was 1100-1200°C., but that some might vaporize at higher temperatures (1400-1450°C.). In dry systems 70-80% of the fluorine was retained in the temperature range 1000-1400°C., but only half as much was retained in the presence of water(84,86).

Reynolds, *et al* (97) heated charges of fluorspar in a tube furnace for periods of 30 minutes in an air stream containing 91% water vapor. No fluorine was lost at 900°C., but losses ranged from 9% at 1000°C. to 92% at 1300°C. Fluorspar was also mixed with an approximately equal weight of silica and was heated both in dry air and in an atmosphere of 91% water vapor. In dry air, no fluorine was lost at 900°C., but the loss ranged from 3% at 1000°C. to 53% at 1300°C. In the presence of moisture, the loss of fluorine ranged from 11% at 800°C. to 91% at 1300°C.

Loss of fluorine in the manufacture of welding flux was reported by Conn(20). When flux ingredients were melted, 50-60% of the fluorine added to the batch was lost. Moisture in the raw materials was found to be responsible, and Conn concluded that hydrolysis occurred. He reported some loss at only 180-250°C., which is a lower temperature than any other reported to produce pyrohydrolysis. He also reported that no loss of fluorine occurred in a dry batch if the temperature was kept below the vitrification range (1180°C.), but that some was lost even from a dry batch if vitrification took place.

Formation of Particulate Fluorides

Information on the nature of particulate fluorides emitted from various processes is almost totally lacking in the literature. Such data on Reactions 17, 18, and 19 as exist have been reported in other connections than atmospheric pollution. The bulk of them are concerned with volatilization of potassium compounds. The volatilization of alkalis from cement kilns and blast furnaces is well known and has been used as a method for recovering potash(4,9,54,55,102,103). When such a material as feldspar (potassium aluminum silicate) is subjected to high temperatures in the presence of calcium compounds, calcium aluminum silicates are formed and the potassium is volatilized in the form of the oxide or of salts. Ignition of the potassium aluminum silicate alone does not produce a change in composition(103).

Anderson and Nestell(4) made a laboratory study of volatilization of potassium in cement manufacture. They considered that the following factors might affect the volatilization:

(1) The temperature
(2) The volume of gas flowing
(3) The intimacy of contact between the gas and the cement mix
(4) The vapor pressure of potassium salts formed

TABLE V

Fluorine Emissions From Various Processes

Process	Process Materials	Process Equipment	Fuel Used	Water Vapor In Gases (%)	Maximum Tempera ture (°C)	Percent of Input Fluorine Emitted	Remarks	Refer- ence.
Calcining phosphate rock (beneficiation)	Phosphate rock	Rotary kiln	Oil	8-10	1090 820	3 Almost nil	Residence time short at maximum temperature	(75)
Calcining phosphate rock (defluorination)	Phosphate rock	Rotary kiln	Oil	13	1400-1450	50-70 75	Residence time = 1 hour Residence time = 2 hours	(14)
Calcining phosphate rock (defluorination)	Phosphate rock, silica	Rotary kiln	Oil	20*	1480-1590	98	Residence time in burning zone = 20-30 min.	(124)
Nodulizing phosphate rock	Phosphate rock	Rotary kiln	Oil Coal CO gas	4-12	1200-1480	20-45	Residence time = 30 min.	(18, 51, 109)
Sintering phosphate rock	Phosphate rock	Dwight-Lloyd Machine	Coke		1400*	30 35-40	Moisture in charge	(49) (18)
Calcining phosphate rock	Phosphate rock briquets	Rotary kiln	Oil Coal CO gas	4-12*	1000-1040	Almost nil		(18)
Calcining phosphate rock	Phosphate rock pellets	Shaft kiln	CO gas Propane-butane	4* 8-12*	1090-1200	14 14		(108)
		Rotary kiln	Oil	8-12*	1150-1180	28		(109)
Defluorinating molten phosphate rock	Phosphate rock, silica	Electric furnace		Low	1600	Small	Melting without further treatment	(14, 25)
		Hearth furnace	Oil	8-12*	1500-1550	84-95	Melting time = 4-25 hrs.	(14)
		Hearth furnace	Oil	8-12*	1490-1595	72-86	Pool depth = 18 in.	(14)
		Electric furnace (for melting) Hearth furnace (for defluorination)	Oil	12	1550-1600	90	Pool depth = 3 in. Heating period = 2 hrs.	(14)
				12	1600	92-96	Pool depth = 1.5-2 in. Heating period = 60-80 min.	(14)
		Shaft furnace	CO gas	4	1430-1540	70		(14)
			Oil	12-14	1430-1540	90 or greater		(14)
Phosphoric acid manufacture	Phosphate rock, coke	Electric furnace		Low	1480*	35 25 20-30		(59) (24) (53)
	Phosphate rock, silica	Blast furnace	Coke		1740-1850	52 30	Abt. 17% of emission in particulate form Abt. 50% of emission in particulate form	(48) (53)
Elemental phosphorus manufacture	Phosphate rock, silica coke	Electric furnace		Very Low	1470*	9.6	Abt. 16% of emission in particulate form	(18)
Calcium-magnesium phosphate manufacture	Phosphate rock, olivine,	Electric furnace		Low	1450-1550	27-33 11	Batch operation Continuous charging	(121)
	Phosphate rock, olivine, silica	Electric furnace		Low	1450-1550	27-57	Batch operation	(121)
	Phosphate rock, olivine	Electric furnace		Very low	1500-1600	10-20	Fusion time = 1-2 hrs. Continuous charging, with unfused material above melting zone	(79)
Manufacture of Rhenania phosphate	Phosphate rock, soda ash, silica	Rotary kiln	Coal	8-10*	1100-1200	8		(51, 120)

(Continued on Page 99)

TABLE V

Fluorine Emissions From Various Processes

(Continued from page 98)

Process	Process Materials	Process Equipment	Fuel Used	Water Vapor in Gases (%)	Maximum Temp. (°C)	Percent of Input Fluorine Emitted	Remarks	Reference
Calcining ironstone	Ironstone	Open heaps	Coal		1100	15-30	Moisture in charge	(16, 39, 40)
		Rotary kilns	Coal	8-10*	1000-1200* Lower	15-20 Small	Temperature not reported	(40)
Steelmaking	Steel, iron ore, limestone fluorspar	Open hearth furnace	Oil or gas	8-10*	1650-1920*	50	Emission given is fraction of fluorine added as fluorspar	(40)
Brick making	Clay	Kiln	Coal	8-10*	1000	30	Part of heat from combustion of organic matter in clay	(6)
Glass making	Silica, soda ash, feldspar, etc., fluorspar, cryolite, or sodium fluosilicate	Tank furnace	Gas	8-10*	1400*	20		(123)
						10		(41)
Roasting zinc oxide fume	Impure zinc oxide containing fluorides	Wedge-type roaster (7 burning hearths)	Coal	8-10*	650	98-99	Residence time = 105 min.	(32)
Calcining topaz	Topaz	Rotary kiln	Oil	8-10*	1480	98-99	Residence time = 70 min. Chemically-bound water in charge	(98)
Manufacture of calcium metaphosphate	Phosphate rock	Combustion chamber and absorp. tower	White phosphorous	10-14	1100	80-85		(18, 21)
Defluorination of superphosphate	Triple superphosphate	Rotary kiln	Oil	5.2-9.8	370-390	78-82	Residence time = 27 min.	(11)
Manufacture of superphosphate	Phosphate rock, sulfuric acid	Mixer and den		18-20	100-115	16-42 30-35	Extreme range Average	(51, 53, 91, 107)

Note: * Values estimated

(5) The dissociation of the potassium compounds to form more volatile materials
(6) The degree of saturation of the gases
(7) Diffusion of the potassium compounds through the interstices of the mix to its surface and from the surface to the main body of the gas stream.

They concluded from their laboratory data that temperature and time of exposure were the determining factors. The minimum temperature for volatilization was 1100°C.; the rate was low up to about 1200°C., but increased sharply between 1200° and 1300°C., and was high from 1300° to 1400°C. The temperature effect was dependent in part upon the material, and volatilization increased with decrease in the size of the clinker. The presence of chlorides (particularly $CaCl_2$) increased the evolution of the potassium. Sodium was driven off almost as readily as potassium, although sodium compounds are less volatile than those of potassium.

Other investigators(55,70) studied the effects of adding materials such as $CaCl_2$ to promote volatilization of potassium by formation of more volatile compounds. Madorsky(70) used CaF_2 as a promoter for removing potassium from wyomingite, a potassium aluminum silicate. The temperature used was 1510°C., and the atmosphere of the electrically heated furnace was presumably dry. Increasing the amount of added CaF_2 up to about 50% excess over the stoichiometric ratio increased removal of potassium, but further increases had little effect. However, the total loss of weight of the charge was greater than the calculated amount of KF, and the discrepancy increased with increase in the amount of CaF_2 added. Madorsky suggested that the additional loss of weight might have been due to liberation of SiF_4 by Reaction 6. However, it appears that AlF_3 might have been formed, as suggested by the data of Nagai and Yoshiura(87,88). The latter studied the effect of CaF_2 additions on the thermal synthesis of calcium aluminates from Al_2O_3 and CaO or $CaCO_3$. When pure $CaCO_3$ and Al_2O_3 were heated with added CaF_2 in a tube furnace(88) the amount of CaF_2 lost increased with increase in temperature, and was greater than in the dry thermal synthesis of calcium silicates. Increasing the amount of added CaF_2 also increased the amount lost. It appears improbable that significant amounts of CaF_2 vaporized. Hence, if water vapor was not present the fluorine can hardly have been evolved except as AlF_3.

On the basis of the foregoing information it appears that appreciable amounts of NaF, KF, or AlF_3 may be volatilized from certain processes. However, their formation should in most cases be of far less importance than pyrohydrolysis in emission of fluorine, since the concentrations of sodium, potassium and aluminum in most process materials are relatively low.

Emission of Fluorine From Various Processes

A considerable body of published information on emission of fluorine from industrial processes exists, though in widely scattered sources. Fluorine concentrations in waste gases have been reported in a number of instances, and values regarded as reasonably reliable are compiled in Table IV. The fractions of input fluorine emitted from a number of processes have also been reported, and are given in Table V along with such process data as were available or could be estimated.

By far the largest source of information is that on defluorination of phosphate rock. Because phosphate rock must be freed from most of its fluorine in order to be suitable for use as fertilizer or livestock feed supplement, extensive investigation of the mechanisms of defluorination has been carried out, mostly by the U. S. Department of Agriculture and the Tennessee Valley Authority. Many of the conclusions can be applied by analogy to other industrial processes.

Defluorination of Phosphate Rock by Calcination

Reynolds and his co-workers (71,97,98,99) carried out an extensive bench-scale investigation of defluorination of phosphate rock by calcination in the presence of water vapor. Samples were heated in platinum boats in an electrically-heated tube furnace, and variables studied included the water content and velocity of the furnace gases, the weight, particle size, and composition of the charge, and the temperature and time of heating. In dry atmospheres (97), comparatively small amounts of fluorine (less than 32%) were driven off at temperatures of 1000-1400°C., but in moist atmospheres the volatilization increased to over 90% as temperatures were increased from 700° to 1400°C. Addition of silica did not have important effects on volatilization of fluorine unless water vapor was also present. In the absence of water, the time of heating at 1200°C. had little effect upon loss of fluorine, but in the presence of moisture the loss increased with time. The volatilization of fluorine increased with increasing water content of the furnace atmosphere but was not affected by substitution of oxygen or nitrogen for air (98).

It was found (98) that in the presence of water vapor small charges gave more complete defluorination because of a higher ratio of directly exposed surface to volume of charge. For large samples volatilization increased with temperature up to about 1425°C., then tended to decrease, apparently because sintering or partial fusion reduced the amount of surface exposed to contact with water vapor. With small samples, volatilization continued to increase to somewhat higher temperatures, probably because the proportionate reduction in exposed area was less.

Reduction in particle size of the samples also increased liberation of fluorine (98), except for the finest particles, which appeared to fuse more readily. When phosphate rock was heated in single-grain layers in the presence of water vapor, fluorine loss generally increased with decrease in particle size (99). Most of the fluorine was driven off in a short period; thereafter, the rate of elimination decreased markedly.

It is probable that at least part of the loss of fluorine from some of the samples heated in dry atmospheres was due to pyrohydrolysis by moisture or chemically-bound water in the charge, or by water formed by combustion of organic matter in the phosphate rock samples. This view is supported by failure of the loss of fluorine to increase with time of heating. Also, when samples were pre-dried at 400-500°C., there was a reduction in the amount of fluorine volatilized during subsequent heating at 1300°C., in a dry atmosphere.

In later tests reported by TVA (14), it was found that the degree of defluorination was increased by increases in both water vapor concentration and velocity of the furnace gases. The rate of defluorination was markedly reduced if as much as 2% of HF was present in gases containing 60% of water vapor, indicating an approach toward equilibrium.

Although the bench-scale experiments described above indicated the principal factors in volatilization of fluorine from phosphate rock, they did not give results which are directly comparable to those obtained in full-scale equipment or processes. During calcination in a device such as a rotary kiln, the charge is continually moved, exposing new surface, and gas velocity is usually greater.

TVA investigated on a pilot plant scale the defluorination of phosphate rock by calcination below the fusion point in a rotary kiln (14). The kiln was oil-fired, and the combustion gases contained about 13% water vapor (see Table V). The extent of defluorination was too low for the desired purpose. Use of coarser charges markedly reduced the rate of defluorination. When the temperature was increased above 1450°C., the charge was partly fused and formed a pasty mass which was impervious to the water vapor, and the rate of defluorination decreased. Increasing the water vapor content had no significant effect upon the degree of defluorination.

The Coronet Phosphate Company developed a process for defluorination of phosphate rock by calcining without fusion (73,124). A large amount of silica (35-45%) is added to the charge, but its action is primarily mechanical. Its function is to prevent coalescence of the low-melting constituents in the charge and to keep the calcined mixture free-flowing and porous, so that the water vapor may diffuse readily to all parts of the mixture. Maust claimed (73) that the fluorine evolved was not in any combination with silica, and that no chemical change involving the silica (except possibly a catalytic action) was involved in the process of defluorination. The accelerating action of SiO_2 according to Reaction 15 may, however, actually be involved. Maust reported that evolution of fluorine began to take place at about 870°C., but did not attain a commercially feasible rate until a temperature in excess of 1320-1370°C. was reached.

Maust proposed three alternative forms of apparatus for carrying out the defluorination: (1) a shaft furnace, (2) a downdraft sintering machine of the Dwight-Lloyd type, or (3) a rotary kiln. In either of the first two devices, the moist gases would be drawn through the charge so as to come into intimate contact with a large exposed surface. In the rotary kiln, the gas stream passes over the surface of the charge, and achieving contact between the moisture-laden gases and the particles of the charge is more difficult.

In the commercial process(124), rotary kilns are employed (see Table V). Extra water vapor is added to the kiln atmosphere through quenching of the hot product in water. The temperature in the kiln ranges from 540-760°C. at the feed end to 1480-1590°C. in the burning zone. About 20-30 min. are required for the charge to pass through the burning zone, and a very high degree of defluorination is attained.

Similar results in thermal treatment of phosphate rock are reported by Volfkovich, *et al*(119).

Beneficiation of Phosphate Rock by Calcination

Before processing, phosphate rock is often dried in oil- or coal-fired rotary kilns at low temperatures (about 150°C.). This treatment is used for elimination of free moisture only(75), and at such low temperatures liberation of fluorine is unlikely. However, where the rock is to be used for manufacture of phosphoric acid by the wet process, calcining at higher temperatures (500-900°C.) is carried out to decompose carbonates, remove organic matter and chemically-bound water, and drive off moisture (75,120). The process in this case is similar to calcination for the purpose of defluorination, except that the temperatures are lower, and some fluorine is evolved. Memminger, *et al* (75) describe calcination in a rotary kiln (see Table V). The charge was maintained at the peak temperature for only a short time, and this was reported to be responsible for the low emission of fluorine, which was about 3% at 1090°C., and almost nil at 820°C. It was reported that SiF_4 was evolved, but no supporting data were given and the existence of SiF_4 was probably assumed.

Agglomeration of Phosphate Rock

In order to produce a change of the proper size for use in electric furnaces, shaft furnaces, or blast furnaces, it is frequently necessary to agglomerate the material by sintering, nodulizing, briquetting, or pelletizing (109). In sintering and nodulizing, the material is raised to a temperature such that particles are fused together. In electric furnace charges, the presence of moisture is objectionable, and sintering, nodulizing, or calcining of briquets or pellets serves to drive off moisture, combined water, organic matter, carbon dioxide, sulfur, and part of the fluorine(18,109). Reported emissions of fluorine are presented in Table V.

In sintering with a Dwight-Lloyd machine, the air drawn through the bed is comparatively dry, but the bed itself is moist; the moisture content is a critical factor in the bed porosity and hence in the rate of sintering(109).

In the calcination of briquets or pellets the size of pieces may have a considerable effect upon the evolution of fluorine. Calcination of pellets in a rotary kiln(18) resulted in higher fluorine losses than did calcination in a shaft kiln(109). In the shaft kiln, use of propane-butane fuel gave a higher water vapor concentration than did the CO originally used but did not increase the removal of fluorine. Possibly some fluorine was reabsorbed by the cooler part of the charge near the top of the shaft.

Defluorination of Molten Phosphate Rock

TVA developed several processes for defluorination of phosphate rock in the molten state(14,25). Elmore, *et al* made an extensive bench-scale investigation of the mechanism of defluorination(14,33). Samples were fused in boats in a tube furnace, and studies were made of the effects of the composition of the charge, the water vapor concentration and velocity of the furnace atmosphere, the temperature, and the depth of the melt. A stream of nitrogen containing various percentages of water, vapor was passed over the surface of the samples. As a result of their investigation, Elmore, *et al*(33), postulated the following mechanism of defluorination:

1. The fluorine diffuses upward through the melt as a compound or an ion.
2. There is no convective circulation in the melt.
3. The concentration at the surface of the melt at any instant is controlled by the rate of upward diffusion of the fluorine constituent.
4. Water vapor reacts with the fluorine constituent at the surface of the melt.
5. The rate of removal of fluorine at the surface of the melt is proportional to its concentration in the surface layer.

It was found that in shallow pools the rate of defluorination was controlled by the resistance at the surface of the melt. The rate was affected little by the temperature in the range 1450-1600°C., but varied directly as the 0.45 power of the water vapor concentration and the 0.3 power of the velocity of the furnace atmosphere. In deep pools, the rate-determining step was diffusion of the fluorine through the melt; the rate was less dependent upon the water vapor concentration and the gas velocity and varied inversely with the square of the depth of the pool and increased with increase in the temperature or increase in the fluidity of the melt. It was concluded that the effect of increase in temperature was primarily to increase the fluidity of the melt and, hence, the rate of diffusion of the fluorine component through the melt. Fluidity could also be increased by addition of a suitable flux (such as silica), and flux content was indicated to be a major factor in determining the rate of defluorination at a given temperature.

In the absence of water vapor, about 10-15% of the fluorine was evolved at 1500°C., but this was believed to be due to presence of a small amount of water in the cylinder nitrogen used. Some defluorination (10-20%) also took place at 1600°C., in a dry nitrogen atmosphere, possibly for the same reason. Although it was considered possible that SiF_4 might be formed (14), thermodynamic calculations were reported to indicate that volatilization of appreciable amounts of SiF_4 at 1600°C., was improbable under the experimental conditions.

Elmore, *et al*, suggested that the exponent of the furnace atmosphere velocity would be greater than 0.3 for velocities in the turbulent flow range (33). The results obtained in the laboratory investigation indicated that satisfactory defluorination could be obtained in furnace atmospheres containing 30% water vapor, However, later results in plant operation(14) showed that satisfactory results could be obtained at a temperature of 1550°C., with furnace gases containing only 8-10% water vapor. In the large furnaces the gas flow was turbulent, and there was probably also convective circulation in the molten phosphate rock, contrary to the conditions in the bench-scale tests made by Elmore, *et al.*

TVA subsequently investigated a number of processes for defluorination of molten phosphate rock(14,25,49), the features of which are summarized in Table V. Melting in an indirect-arc electric furnace without further treatment resulted in little defluorination. Melting in a reverberatory hearth furnace gave results dependent in part upon pool depth; shallow pools gave the most effective defluorination. Relatively rapid defluorination was obtained when the flames from the burners impinged upon the melt and agitated it.

TVA later developed a process for defluorination which employed an oil- or gas-fired shaft furnace(14,49). It was expected that as the charge melted in the furnace shaft it would form thin films and droplets, favoring rapid defluorination. It was postulated(14) that the molten material flowed in thin films to the hearth as soon as it reached a temperature at which it was sufficiently fluid, and that it was not further heated or defluorinated after reaching the hearth. Exposure time was therefore relatively short, and the temperature of the melt was determined primarily by the chemical composition and was normally only slightly above the melting point. In the hearth furnace increasing the fluidity of the charge by addition of flux increased the extent of defluorination. In the shaft furnace, increasing the flux content of the charge lowered the melting temperature but did not necessarily increase the degree of defluorination.

Blast Furnace Smelting of Phosphate Rock

In the phosphate blast furnace(48), the concentration of water vapor in the hot blast air is relatively low, and consequently conditions are not highly favorable to pyrohydrolysis of the calcium fluoride or fluorapatite despite the high temperatures existing in the combustion zone. Moisture in the charge itself should be largely removed by the hot gases rising through the furnace shaft, before the charge reaches a temperature high enough for significant defluorination. Fluorine emissions have been reported to be relatively low (see Table V), and to consist to a considerable degree of particulate fluorides(48,53,96).

In an early paper, Reynolds and Jacob(96) calculated the volatilization of fluorine from phosphate blast furnaces as 16-27%, depending in part upon the basis of calculation. They also calculated the loss of fluorine from electric furnaces *(see below)*, and concluded that the loss in this case was lower than in the blast furnaces because of the smaller amount of water vapor present. They reported that the fluorine appeared to be mainly in the form of SiF_4, but gave no supporting data; their later work, cited above, does not support this early report. They reported that Russian investigators smelting phosphate rock in a fuel-fired shaft furnace at 1100-1540°C. found fluorine losses of 40.6-97.5%. In this latter method, which appears similar to that reported by Hignett(14,49), the water vapor concentration should have been higher than in the blast furnace.

Jacob, *et al* (53), later reported that about 30% of the fluorine was emitted from the blast furnace, and that about half of the emission was in the particulate form. The most complete data are those of Hignett(48), which indicate a fluorine emission of 52%. Of the fluorine emission about 17% was in the particulate form. The fine dust and fume contained relatively large amounts of sodium and potassium and had a fluorine content two or three times as high as that of the original material, so that the fine particulate fluoride may have been largely NaF and KF.

Electric Furnace Smelting of Phosphate Rock

In the electric furnace, the water is limited to that present in the materials charged or in the atmospheric air present in the furnace atmosphere. Consequently, the opportunity for pyrohydrolysis of the fluorides is limited despite high temperatures. Since the presence of moisture increases consumption of power and electrodes, calcining, sintering, or nodulizing of the phosphate rock charge is usually practiced(18,109).

The fraction of fluorine volatilized in electric furnaces used in producing phosphoric acid has been reported (24,59) to be 25-35% (see Table V). Reynolds and Jacob(96) computed values of 7-13%, depending upon the basis of calculation. Some of the variation in reported emissions is probably due to differences in the moisture content of the charge material. In furnaces producing elemental phosphorus, prevention of air inleakage into the furnace is critical(18), and the amount of water vapor present may be lower than in most furnaces producing phosphoric acid. Burt and Barber(18) have reported a material balance on a TVA furnace.

Both Burt and Barber(18) and Klugh(59) reported that SiF_4 was volatilized, but gave no supporting data. The hypothetical case given above, for which equilibrium concentrations of SiF_4 and HF were calculated, was based primarily on conditions in an electric furnace, and supports the view that such gaseous fluoride as is formed is HF formed by reaction of the fluoride with the small amount of moisture present in the furnace atmosphere or charge. However, at electric furnace temperatures the vapor pressure of molten silica itself is high and silica fume is formed(24). Under these conditions differentiation between SiF_4 and HF by sampling of the off-gases would be very difficult.

Manufacture of Calcium Magnesium Phosphate

Processes were developed for production of calcium magnesium phosphate by fusion of phosphate rock with olivine, a magnesium iron silicate(78,79,122). The fusion was carried out in electric furnaces, so that conditions were similar to those in the electric furnace production of phosphoric acid (see Table IV).

In the original pilot scale investigation reported by Walthall and Bridger (122), batch operation was employed.

	Input	Output		
	Phosphate Rock Nodules	Slag	Precipitator Dust	Phosphorus Condenser Sludge
Concentration of F (%)	2.2	2.6	5.9	. . .
Concentration of K_2O(%)	. . .	. . .	16.2	. . .
% of Total F	100	91.4	1.5	9.1

Charges were melted in about 30 min., and the melt temperature reached 1450-1550°C. The fraction of the fluorine volatilized ranged from 27-33%. When additional silica was added, the fluorine volatilization was generally somewhat greater, and ranged from 27-57%.

In another experiment, continuous charging was employed, and a mass of unfused material was maintained above the surface of the melt, primarily to absorb any liberated P_2O_5 vapors. Under these conditions only 11% of the fluorine was volatilized.

In these tests the moisture present in the furnace atmosphere was presumably only that in atmospheric air. Walthall and Bridger did not report any pretreatment of the phosphate rock, and the latter probably contained both free and combined water which could have been responsible for most of the observed fluorine volatilization. In the experiment with continuous charging, the charge was probably partly dried by heat from the melting zone before it was itself fused. In addition, some of the fluorine may have been reabsorbed by cooler parts of the charge material.

In later commercial scale operation of this process reported by Moulton(79), continuous charging was also employed. The charge materials were dried in an oil-fired rotary drier in order to avoid the high power and electrode consumption caused by moisture in the furnace charge. Only 10-20 % of the fluorine was evolved (see Table V). Moulton stated that water vapor was present in the vent gases, and suggested that the fluorine evolved was in the forms of HF and H_2SiF_6. However, the latter, if present, was probably formed by a secondary reaction between the HF, silica, and water vapor in cooler parts of the vent system.

Moulton also reported laboratory investigation of this process(78). The charge material was dried at 105°C., then placed in crucibles and fused in a nitrogen or hydrogen atmosphere in a tube furnace. The charge began to fuse about 2½ minutes after being placed in the furnace, and the fusion time was about 10 minutes. Samples were held in the molten state for varied periods of time at temperatures ranging from 1460-1730°C. A vigorous evolution of gases during fusion was reported. Moulton also reported that fluorine in excess of a ratio of 0.56 mole of fluorine/mole of P_2O_5 was volatilized, and that more was volatilized in a hydrogen atmosphere and, in some cases, in highly siliceous melts. The emission of fluorine was reported to be dependent upon the P_2O_5 content (and possibly, the alumina content) of the melt, and not to be increased by long fusion times or by increase in temperature up to 1470°C. Although no explanations for this observed behavior were offered, some of the loss of fluorine may have been due to presence of moisture or combined water in the charge which was not removed by the preliminary drying. The failure of the loss of fluorine to increase with fusion time is consistent with this hypothesis.

Manufacture of Rhenania Phosphate

Rhenania phosphate is produced by calcining a mixture of phosphate rock, soda ash, sand, and sometimes powdered coal in rotary kilns at temperatures below the fusion point (120,121). The function of the powdered coal is primarily to prevent excessive agglomeration of the charge. The maximum temperature is 1100-1200° C. and the residence time in the kiln is about 2 hrs.

The net reaction is claimed to be (120,121):

$$\begin{gathered}2\,Ca_{10}(PO_4)_6F_2 + \\ 6\,Na_2CO_3 + 5\,SiO_2 = \\ 6(Na_2O.2\,CaO.P_2O_5) + \\ 4\,(2\,CaO.\,SiO_2) + \\ SiF_4 + 6\,CO_2.\end{gathered} \tag{22}$$

The SiF_4 is reported (120) to be decomposed to SiO_2 and HF by reaction with water vapor. Water vapor is considered necessary to remove the fluorine and is introduced into the kiln in some cases(120). Some sodium fluoride is formed, and additional sodium carbonate is required with phosphate rock containing large amounts of fluorine(121). The evolution of fluorine is markedly influenced by the conditions of processing; in the manner that the process is operated in Germany, only about 8% is volatilized(51).

In view of the other data available, it is unlikely that SiF_4 is formed according to Reaction 22, but is more probable that HF is volatilized directly according to Reaction 15. In addition, NaF is formed by Reaction 20 (or a similar reaction) and some is probably volatilized directly.

Free energy data for Reaction 20 are lacking in the temperature range 1100-1200°C., but the trend of data for lower temperatures indicates that the free energy should have a fairly large negative value at the operating temperatures, favoring formation of NaF. The formation of NaF may, however, repress formation of HF, since NaF is more resistant to hydrolysis than is CaF_2.

Manufacture of Calcium Metaphosphate

TVA has produced calcium metaphosphate by the reaction of phosphate rock with P_2O_5 vapor at high temperatures(13,21,121). The principal reaction is represented by the equation.

$$\begin{gathered}Ca_{10}(PO_4)_6F_2 + 7\,P_2O_5 + H_2O = \\ 10\,Ca(PO_3)_2 + 2\,HF.\end{gathered} \tag{23}$$

The P_2O_5 is formed by burning white phosphorus in air in a combustion chamber. Pulverized rock phosphate is blown into the chamber with air and reacts with the P_2O_5 to form molten calcium metaphosphate. The gases leave the chamber through a tower packed with lump or briquetted phosphate rock, which absorbs the P_2O_5 that has not reacted with the pulverized rock. The operating temperature is somewhat above 1000°C., and about 80% of the fluorine is volatilized. Cooling water is injected into the combustion chamber (13) in amounts such that the water vapor content of the furnace atmosphere is about 10-14%. The fluorine is emitted in the form of HF(50).

Tarbutton, *et al*(113) studied the reaction of P_2O_5 with CaF_2 on a laboratory scale. At 500-1000°C. the volatile products consisted mainly of POF_3 and PF_3, with some HPO_2F_2 and HF. The reaction reported to be most nearly in agreement with the observed results is

$$\begin{gathered}3\,CaF_2 + 4\,P_2O_5 = \\ 2\,POF_3 + 3\,Ca(PO_3)_2.\end{gathered} \tag{24}$$

The formation of HPO_2F_2 and HF was believed to be due to hydrolysis of POF_3 by a small amount of water present in the charge:

$$POF_3 + H_2O = HPO_2F_2 + HF. \tag{25}$$

On the basis of these data, Reaction 23 may be considered to consist of a step similar to Reaction 24, followed by a hydrolysis of the POF_3 to form HF.

Tarbutton, *et al* reported that when P_2O_5 reacted with phosphate rock at

700°C. most of the fluorine appeared to be volatilized as SiF_4, but gave no supporting data.

Processing of Zinc Oxide Fume

Ellerman(32) has reported the roasting of zinc oxide fume to remove fluorine. The zinc oxide is fumed from copper smelter reverberatory slag and is collected in a bag filter. The impure oxide contains about 0.18% of fluorine, which is objectionable in the subsequent electrolytic production of zinc.

The roasting is carried out in a coal-fired Wedge-type roaster having 7 burning hearths. Ellerman presents data showing that most of the fluorine is removed in the first 2 hearths, after which the rate of elimination drops sharply. About 98-99% of the fluorine is driven off. In tests, the elimination of fluorine was increased by increase in the roasting temperature up to about 650°C.; thereafter, further increases in the temperature did not increase the rate or extent of fluorine removal.

Although Ellerman did not indicate that the removal of fluorine is produced by pyrohydrolysis, the process is analogous to the defluorination of phosphate rock. Lower temperatures are effective in defluorinating the impure zinc oxide than in treating phosphate rock, since zinc fluoride is more readily hydrolyzed than calcium fluoride(28).

Calcining Topaz

Production of mullite ($3\ Al_2O_3 \cdot 2\ SiO_2$) for use in refractories by calcination of topaz was studied by a number of investigators, although commercial application of the method was apparently never developed. The formula for topaz may be given(10) as $[Al(F, OH)]_2\ SiO_4$. Fluorine and hydroxyl are isomorphous and appear in variable relation to one another. When topaz is calcined, the fluorine, combined water, and some silica are eliminated, and mullite is formed. Some investigators(10,17,68,111) considered that SiF_4 was liberated, although Burgess(17) believed that HF was also formed. Finely divided silica was reported to be evolved (17,93,111), but this may have been formed by direct volatilization of silica, as reported by Eitel(31).

Pole(93) studied calcination of topaz in a rotary kiln (see Table V). Essentially complete defluorination was attained at a temperature of 1480°C. Although conditions were similar to those in calcination of phosphate rock, the evolution of fluorine as HF in this case was probably increased by the presence of combined water in the topaz molecule.

Manufacture of Superphosphate

The volatilization of fluorine in the manufacture of superphosphate has been discussed fairly extensively in the literature(51,53,91,106,107,120,126). The principal reactions involved have been discussed above. Whynes(126) reported that experiments with a small laboratory mixer showed that no HF, but only SiF_4, was evolved, but gave no details. The equilibria discussed above indicate, however, that a small proportion of HF should be present, and it would appear possible for some HF to escape directly from the reaction mixture. Both Sherwin(107) and Whynes(126) report that mists containing H_2SiF_6 are formed by absorption of SiF_4 in fog formed in the saturated den and mixer gases.

The fraction of the fluorine which is evolved depends in part upon the materials used and the conditions of the process, and ranges from about 16 to 42% (see Table V). Atmospheric pollution by fluorides from superphosphate plants has been reported frequently in the literature, and numerous control systems have been developed(40-46,77,91,107).

Defluorination of Superphosphate

In some cases it is necessary or desirable to remove additional fluorine from superphosphate(11,37). In one process(120) the phosphate rock is treated with sulfuric acid, then heated to 200-300°C., driving off about 90% of the fluorine. Heating of superphosphate with or without added water vapor has been studied on a laboratory scale by Fox, *et al*(37), and on a pilot plant scale by TVA(11). Probably the process may be considered as an acid distillation; temperatures employed are too low in most cases for pyrohydrolysis to be very important.

Aluminum Reduction Plants

Some of the major instances of fluorosis in livestock have occurred in the vicinity of aluminum reduction plants(1,27,65,100,101). The source of the fluorine is the molten cryolite bath in which the dissolved alumina is electrolytically reduced. The mechanism by which the fluorine is liberated is a matter of dispute(27). It has been claimed(27) that SiF_4 is formed by reaction of the cryolite with silica present in the bath or in the carbon electrodes. The amount of silica present in the bath is deliberately kept as low as possible. According to other authorities(27,66), a portion of the cryolite is volatilized and either forms a fume or is partly hydrolyzed by moisture in the air to form HF; this latter explanation is in closer agreement with the properties of NaF and AlF_3 discussed above.

Both gaseous and particulate fluorides are formed(66,128); the two forms are reported to be about equal in quantity(66). Some of the particulate fluoride is undoubtedly mechanically entrained, but fumes of both NaF and AlF_3 can be formed, and are reported to be of very fine particle size(66).

The surface of the bath is covered by a crust of alumina which must be periodically broken to permit escape of gases and addition of alumina(129). Carbon dioxide is liberated and carries some of the fluorides with it (66,129). At the bath temperature (about 1000°C.) the vapor pressures of both NaF and AlF_3, are significant. The principal opportunity for contact with water vapor occurs as the liberated vapors of NaF and AlF_3 are mixed with air above the cell, or *pot.* Since mixing of the air with the vapors produces rapid cooling, only a short period of time should elapse in which temperatures remain high enough for pyrohydrolysis to occur, and the water vapor concentrations are relatively low. Quenching of the vapors by the cooler air also produces the fume. This probably explains the relatively low proportion of gaseous fluoride found; that the amount formed is as great as it is, is probably due to the susceptibility of AlF_3 to hydrolysis.

Drinker and Hatch(29) report that most of the fluoride evolved is NaF. However, Fig. 1 shows that AlF_3 is more volatile. Pearson(89a) states that volatilization losses are greater for AlF_3 than for NaF. It is therefore necessary to add AlF_3 as well as cryolite to the pots as make-up. Martin and Nelson(72) report that production of one ton of aluminum requires consumption of 50-60 lbs. of cryolite and 70-80 lbs. of AlF_3.

Both Pearson(89a) and Kameyama, *et al*(56a) report that considerable amounts of carbon tetrafluoride, CF_4, are formed in aluminum reduction furnaces. This compound can be expected to be extremely inert and non-toxic.

There are apparently no published data giving the actual emission of fluorine from aluminum reduction operations. The data of Martin and Nelson indicate consumption of cryolite and AlF_3 equivalent to 74-87 lbs. of fluorine/ton of aluminum produced; a substantial proportion of this is probably lost by volatilization.

Calcining of Ironstone

In 1948 Blakemore, *et al* (6) reported fluorosis in cattle in Lincolnshire, England, resulting from calcination of ironstone ore. The disease was identified in 1946, after wartime expansion of operations. This is the first reported instance of fluorosis resulting from iron and steel manufacture.

Calcining was carried out to reduce the water content of the ore and to decompose carbonate. The ore was mixed with coal and heaped into ridges, which were then fired. Maximum temperatures reached at least 1100°C. The ironstone was reported to contain 1200 ppm. of fluorine, and the coal 100-160 ppm. Blakemore, *et al* reported that 75% of the fluorine was emitted during calcining. However, government investigators later had to resort to more elaborate sampling methods (39,40), and concluded that the average emission of fluorine was about 30 percent.

Government investigators also studied kiln calcination of ironstone (40). In the Midlands, fluorine losses were reported to be 15-20% (see Table V). In the North of England, where calcining temperatures were lower, emission of fluorine was said to be trivial. Actual kiln temperatures were not reported.

Laboratory experiments were claimed (40) to show that the emission of fluorine was largely a function of temperature. Samples of a Cleveland ironstone containing 950 ppm. of fluorine were calcined for 3½ hrs. at various temperatures. No fluorine was emitted at 600°C., but 28% was driven off at 750° and 90% at 1050°. The effect of water was not considered, but the analogy to calcination of phosphate rock is obvious. The proportion of fluorine emitted in plant-scale calcination was in the same range as that for sintering or nodulizing phosphate rock.

Manufacture of Steel by the Open Hearth Process

The largest use of fluorspar is as a flux in the manufacture of steel in open hearth furnaces. The quantity used varies widely in different plants, but averages about 6.5 lbs./ton of steel produced (80). Roholm (100) and MacIntire (69) have both suggested that steel manufacture may emit large quantities of fluorine. However, fluorosis in livestock produced by this source has been reported only recently (40-46), in the vicinity of a steel plant in England. More recently, a similar instance has been reported in the United States.

British government reports indicate that about half of the fluorine added as fluorspar is emitted (40,41) The form of fluorine emitted is reported to be HF (40) or HF or SiF_4 (41). An extensive investigation appears to be under way (40-46), but few details have been given. The situation in the open hearth steel furnace is analogous to that in the hearth furnaces used in defluorinating molten phosphate rock and mechanism of liberation by pyrohydrolysis should be the same also.

Eitel (31) reviews a report on volatilization of fluorine from open hearth slags; this claimed that in siliceous melts part of the fluorine is evolved as SiF_4, but that in basic slags the CaF_2 is retained. In view of the equilibria calculated above, the emission of SiF_4 is of less importance than that of HF, and even in basic slags fluorine can be readily liberated by pyrohydrolysis.

Members of the U. S. Public Health Service sampled effluents from an open hearth furnace at Donora, Pa., following the air pollution disaster at that city (105). The emission of fluorine was reported to be very small. However, the amount of sampling reported was very limited and it is not clear from the procedures described that all of the fluorine which may have been in the samples was accounted for. The fluorine emissions reported by British sources appear to be more reliable, and the actual emissions from the Donora plant were probably much higher than reported. However, no evidence of any fluorine injury to humans or livestock in the Donora area was found (105).

Manufacture of Brick and Pottery

Fluorine has been reported to be emitted during the manufacture of brick (6,100,101) and pottery (26). Roholm (100,101) cites a report of damage to a wood by fluorine from a brickworks. Blakemore *et al* (6), reported fluorosis in cattle in the vicinity of a brickworks in Bedfordshire, England. In the latter case, the clay used in brickmaking contained 450-550 ppm. of fluorine on the dry basis and about 10% of organic matter. The wet bricks were charged to the kilns and brought up to the ignition temperature, after which they were fired by the combustion of the organic material in the clay. About 30% of the fluorine was driven off.

In laboratory tests (6), dry clay was heated in an electric furnace at different temperatures. Heating for 30 min. at 300°C. distilled off oil from the organic matter but drove off no fluorine, and no significant fluorine loss occurred as a result of heating for 1 hr. at 500°. About 5% of the fluorine was evolved by heating at 700-800°, and 86% was volatilized by heating for 2 hrs. at 1000°.

Blakemore, *et al* considered that the fluorine was probably volatilized as SiF_4. However, pyrohydrolysis of the fluorides in the clay by water from combustion of the organic matter is more likely to have occurred.

Manufacture of Glass and Enamel Frit

In the manufacture of glass and enamel frit, fluorspar, cryolite, or sodium fluosilicate may be used as fluxes or opacifiers (124). It has long been known that fluorine is lost in melting of glass and enamel batches, but the form in which it is lost has been the subject of much dispute (7,31). Earlier workers reported that SiF_4 was evolved by Reactions 6 or 7 (7). Weyl (124) considers it surprising that any fluorine should be retained in glass in view of the volatility of SiF_4. However, Blau and Silverman (7) reviewed the literature and concluded that many earlier investigators had made invalid assumptions in calculating loss of fluorine. They themselves produced glasses with NaF or CaF_2 added to the batches, and found that less than half of the fluorine lost could be accounted for as NaF, CaF_2, or SiF_4. They concluded that Reaction 15 was a more likely mechanism of liberation, and that if SiF_4 were formed it probably reacted with water vapor before leaving the melt. They also considered that F_2 or OF_2 might be formed, but these products are unlikely in view of the extreme reactivity of the materials concerned.

Agde and Kraus(2) concluded that SiF_4 was not formed, but that NaF and AlF_3 added might be sublimed, or HF might be formed in the presence of moisture. Mialki(76) concluded on the basis of X-ray studies that SiF_4 was not evolved, but that HF and NaF were. Nagai, *et al*(83) reported that little SiF_4 or BF_3 was evolved, and that the fluorine escaped chiefly as NaF and F_2; formation of the latter is highly improbable.

The fraction of the fluorine lost in producing a batch of glass in the usual manufacturing operations is reported to be about 20%(124). Loss of fluorine in manufacture of enamel frit is reported by one source, but without much confidence, to be about 10%(41). In tank-type furnaces, the situation is again analogous to that in the hearth furnace used in defluorinating phosphate rock, and the mechanism of liberation of fluorine as HF should be similar. When Na_2SiF_6 is used as flux, SiF_4 can be formed according to Reaction 5, but is probably hydrolized rapidly to HF by the moisture in the combustion gases.

In the manufacture of enamels, which are low-melting glasses, fluorides are used in considerable quantities. Damage from fluorine emissions due to manufacture of enamel and enamel frit has been reported frequently(6,15,16,41-46). Fluorosis in cattle has been reported in both Britain and the Netherlands (6,16,41-46), as well as damage to vegetation and etching of glass in the vicinity of the plants.

Bruins(15) reported that the least fluorine emission occurred when fluorspar was used as flux, that cryolite gave a higher fluorine emission, and sodium fluosilicate the highest. This behavior is consistent with the known properties of the three materials. BF_3 was also reported to be formed, although it appears unlikely that this could be detected even if initially formed. Bruins reported that the fluorine was present as solid compounds as well as in water droplets and as gases. Distinction between gaseous and particulate forms was difficult. Unless condensation of moisture was avoided in sampling, most of the fluorine was found in the condensate.

Production of Lead, Zinc, and Copper

Apparently there have been no recognized instances of damage to plants or livestock caused by emission of fluorine from smelting of lead, zinc, or copper. Roholm(100) and Davenport and Morgis(27) cite early European literature, which indicates that damage from fluorine released from copper and zinc smelting may have occurred in Germany in the latter half of the 19th century. It is not unlikely that considerable emission of fluorine from non-ferrous smelting has since occurred elsewhere, but that any damage resulting has been masked by that produced by other agents, such as sulfur dioxide and arsenic.

Fluorspar is known to be associated frequently with the principal ores of lead, zinc, and copper, such as galena, sphalerite, and chalcopyrite(58,80). Truchot(117) reported that sphalerite nearly always contains some CaF_2, ranging from traces up to 0.3%. Some American zinc ores are reported to contain fluorine(35). Where sulfide ores are used as the source of sulfur dioxide in sulfuric acid manufacture, the fluorine compounds volatilized may damage plant equipment, such as lead or silica tower linings and packings(35,117). In contact sulfuric acid plants the fluorine compounds are removed from roaster gases by washing(35).

It is possible that modern ore concentration methods may reduce the quantity of fluorine in ores, prior to smelting, and if smelter gases are washed and used in sulfuric acid manufacture little fluorine should be emitted to the atmosphere. However, if waste gases are vented directly to the atmosphere significant amounts of fluorine may be discharged. The common processes, such as sintering, calcining, roasting, and smelting in blast furnaces or reverberatory hearth furnaces are all comparable, with respect to fluorine emission, to processes which have been described above.

Manufacture of Cement

It has been reported that cement manufacture may contribute some fluorides to the atmosphere(52). However, no proven instances of resulting damage have been reported, although alleged in at least one case(74). Huffman(52) states that the fluorides are emitted mostly as dusts.

Fluorides may be present in both the clay and the limestone used in cement manufacture. The conditions in a cement kiln are generally favorable to formation of HF by pyrohydrolysis. However, the heavy loading of lime dust in the kiln gases should also favor conversion of HF to CaF_2 in the cooler zones of the kiln. It is therefore probable that the major part of the fluorine emitted is in the particulate form. A considerable amount of the particulate fluoride may be KF or NaF formed by Reactions 18 and 19.

Ross and Merz(103) report a process used at one time for recovery of potassium, in which CaF_2 was added to the kiln charge. The potassium was largely volatilized as KF and recovered in an electrostatic precipitator.

Fluorides, such as CaF_2 and $MgSiF_6$, are sometimes used in cement manufacture to act as mineralizers and promote clinkering(31,58). In such cases, increased emission of fluorine can be expected.

Manufacture of Beryllium

Fluorides are used extensively in the manufacture of beryllium(27,62). Since both the beryllium and the fluorides are toxic, a definite industrial hygiene problem exists among workers in the industry. Danger to persons outside of the plant area has apparently been due, however, to the beryllium rather than to the fluorides.

Founding of Aluminum and Magnesium

In foundries producing aluminum and magnesium or their alloys, the fluxes used frequently contain fluorides such as cryolite or calcium fluoride(3). Furnace practice in aluminum foundries is described by Allen, *et al* (3) and by Jenny(56). Allen, *et al* present some data on concentrations of fluorine in waste gases from open hearth furnaces used in melting aluminum (see Table IV).

In casting magnesium, fluorides are frequently used as oxidation inhibitors(27,126); the fluorides have been considered mostly from the standpoint of danger to workmen in the working areas.

Combustion of Coal

Various investigators have reported the presence of small amounts of fluorine in coal(8,19,22,23). Crossley (22,23) analyzed coals from all the British coalfields and found fluorine contents ranging from 0-175 ppm.

Bradford[8] and Churchill, *et al*[19] report fluorine contents ranging up to 295 ppm. in American coals. Crossley[22] reported that there appeared to be a correlation between the fluorine and phosphorus contents of coals, and concluded that the fluorine was probably present as fluorapatite. Bradford[8] did not, however, find definite evidence of such a correlation.

Crossley ashed coal samples in a muffle furnace, and found that they lost fluorine progressively from 475-1000°C. Combustion appeared to liberate all of the fluorine, although Bradford has since reported that some of the fluorine remains in the ash. Crossley also coked coals in a test apparatus, and found that about 15-50% of the fluorine was volatilized at 1000°. Steaming the coal at 1000° liberated additional fluorine. Crossley concluded that coking alone at 1000° would liberate only about 30% of the fluorine, but that steaming might release 75% or more. These results again indicate pyrohydrolysis as a mechanism of liberation.

Fluorine in coal must contribute to the presence of fluorides in the atmosphere, but there is no evidence that the resulting concentrations are significant from the standpoint of development of fluorosis or damage to vegetation. Churchill, *et al*[19] found fluorine concentrations in vegetation in a Pennsylvania area which were high enough to be potentially dangerous to livestock[61], and suggested that combustion of coal may have been partly responsible. However, other sources of fluorides in the area may have been much more important contributors.

Welding

Fluorides in welding fumes constitute an industrial hygiene problem rather than an air pollution problem. However, some reported data on welding fumes[30,36,114,116] are of interest from the standpoint of mechanisms of liberation.

Welding electrodes sometimes employ coatings containing considerable amounts of calcium fluoride. Arc temperatures may exceed 3000°C.[114]. Investigators[30,114,116] have reported that little gaseous fluoride appears to be formed, but that much of the fluoride in the fume is water-soluble. Drinker and Nelson[30] report that coatings for stainless steel electrodes may contain considerable moisture, but found no HF in the products from burning electrodes. Soluble fluorides could result from formation of KF and NaF from reaction of the CaF_2 with potassium and sodium silicates present in the coatings.

Summary

Thermodynamic considerations and a review of the literature indicate that the principal mechanism of liberation of fluorides in high temperature processes is pyrohydrolysis, which results in formation of HF. The principal variables in pyrohydrolysis in most industrial processes appear to be the equilibrium of the reaction, the water vapor concentration in the process atmosphere, and the factors determining mass transfer. Reaction rates appear to be generally high, although little information is available.

Significant formation of SiF_4 appears to be limited to cases involving thermal decomposition of fluosilicates or reaction of fluorides and silica with acids at relatively low temperatures.

Formation of volatile metal fluorides may be a significant mechanism of liberation in some cases, but is generally of less importance than pyrohydrolysis.

By analogy to known cases, such as are presented in Table V, it should be possible to make order-of-magnitude estimates of the probable fluorine emission from a given process if the quantity of input fluorine is known or can be estimated.

Acknowledgment

The author wishes to express his gratitude to Aluminium Laboratories, Ltd. for permission to use its unpublished data on hydrolysis of AlF_3.

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Cost Estimates of Liquid-Scrubbing Processes for Removing of Sulfur Dioxide from Flue Gases*

J. H. FIELD, L. M. BRUNN, W. P. HAYNES, and H. E. BENSON
Central Experiment Station, Bureau of Mines, U.S. Department of the Interior
Bruceton, Pa.

Rising consumption of fuels of relatively high sulfur content, especially in heavily populated areas, has caused growing concern over the possibility of air pollution by sulfur dioxide. This problem undoubtedly will become more acute in the near future, since a large increase in the usage of sulfur-containing fuels is anticipated for the generation of power and other uses. The Federal Government, by Public Law 159, authorized the Department of Health, Education, and Welfare to conduct research on air pollution. This study of the cost of removing sulfur dioxide from flue gases by existing liquid-scrubbing processes has been prepared by the Bureau of Mines in cooperation with the Department of Health, Education, and Welfare as a part of the air-pollution program.

Three liquid-absorption processes using, respectively, a limestone slurry, ammonia liquor, and a solution of sodium sulfite, were chosen. They have been used either commercially or have been studied thoroughly on a pilot-plant scale. The purpose of this estimate is to determine present-day costs of these processes for removing sulfur dioxide from flue gases. These cost figures will also serve as a basis for comparison with other processes being considered for sulfur dioxide removal.

Removal of the sulfur dioxide from a coal-burning power plant of 120,000-kw. capacity was chosen as a base case. A low-sulfur coal of 1.5 wt.-% and a high-sulfur coal of about 5 wt.-% are considered. Coal consumption of 1 lb./kw. hr. was used, the hourly coal requirement being 60 tons. The flue-gas volume was assumed to be 20,000,000 standard ft.^{3}/hr., with sulfur dioxide concentrations of 0.083 and 0.30% for the low- and high-sulfur coal, respectively. Recently constructed power plants operate more efficiently and use less fuel and excess air than the values considered in this estimate. Obviously the removal of sulfur dioxide in such plants would be more favorable, because the quantity of flue gas and sulfur compounds emitted is lower than those shown for the same generation capacity.

Cost estimates have been made for removing 90% of the sulfur dioxide from gases of both concentration and also for 70% removal from the gas of 0.30% sulfur dioxide content. While it may be unlikely that flue gases with concentrations of less than 0.10% of sulfur dioxide would require purification, an estimate has been included for the low sulfur dioxide content, because data are available for a commercial British plant employing the limestone process at these conditions.

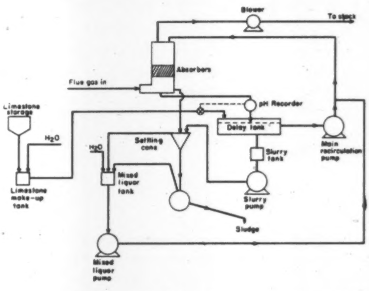

Fig. 1. SO_2 removal by the nonregenerative limestone process.

Description of the Processes

The Nonregenerative Limestone Process

The nonregenerative limestone process was the first non-effluent process used on a commercial scale to lower the sulfur dioxide content of flue gas to extremely low limits.

The commercial plant using limestone was operated by Howden-ICI in England to remove about 90% of the sulfur dioxide from flue gas containing 0.1 to 0.2% of this component. Application of the limestone process at the Fulham power station proved it to be highly efficient.[(1)] Sulfur dioxide is removed from the gas by a neutralizing reaction with a slurry containing about 5 to 10% of limestone or lime as shown by the equations:

$$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2 \qquad (1)$$
$$CaO + SO_2 \rightarrow CaSO_3 \qquad (1\text{-}a)$$
$$CaSO_3 + \tfrac{1}{2} O_2 \rightarrow CaSO_4 \qquad (2)$$

Lime is the preferable material because it is usually more reactive, but in most instances the higher cost of lime makes its use prohibitive. Both calcium sulfite and calcium sulfate are formed by the reaction of sulfur dioxide with limestone, and a sludge containing these materials, as well as some ash, is discharged from this process. This sludge is a waste product and is disposed of.

A schematic flowsheet of the limestone process is shown in Fig. 1. Flue gas at 120°C. passes through distribution chambers to the scrubbing towers, which are connected in parallel. The towers contain wooden grids to provide good contact of gas and liquid, with a minimum of pressure drop. The gas leaves the scrubbers at 50°C., and fans are employed to overcome the loss of head resulting from the scrubbing operation. A slurry of pulverized limestone is pumped to the top of the absorbers, flows downward countercurrent to the gas, and is passed to delay pits. The slurry is held here to permit the growth of crystals. Overflow from the delay tanks is returned to the absorbers after makeup limestone is added. The more concentrated slurry leaving the bottom of the delay tanks flows to cone thickeners and rotary filters in which a sludge of calcium sulfite and sulfate is separated for disposal.

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* Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

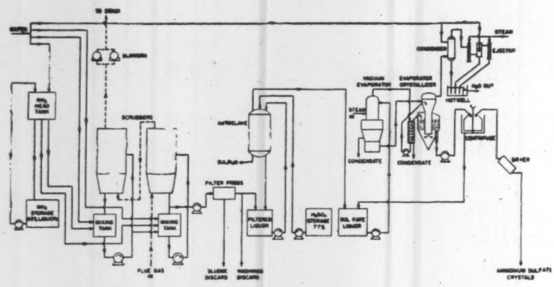
TO STACK
WATER
BLOWERS
NH₃ HEAD TANK
NH₃ STORAGE
SCRUBBERS
MIXING TANK
MIXING TANK
FLUE GAS IN
FILTER PRESS
SLUDGE DISCARD
WASHINGS DISCARD
AUTOCLAVE
SULFUR
FILTERED LIQUOR
H₂SO₄ STORAGE 77%
SULFATE LIQUOR
VACUUM EVAPORATOR
EVAPORATOR CRYSTALLIZER
STEAM IN
CONDENSATE
CONDENSATE
CONDENSER
EJECTOR
STEAM
H₂O OUT
HOTWELL
CENTRIFUGE
DRYER
AMMONIUM SULFATE CRYSTALS

Fig. 2. Ammoniacal liquor process for removal of sulfur dioxide.

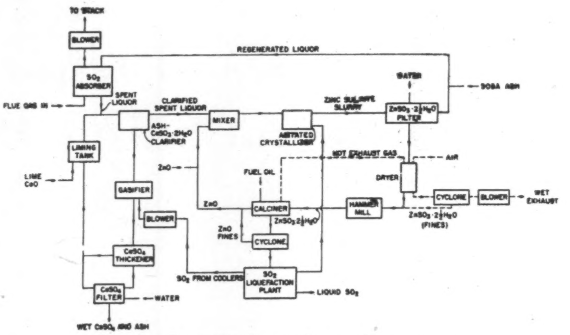
TO STACK
BLOWER
REGENERATED LIQUOR
SO₂ ABSORBER
FLUE GAS IN
SPENT LIQUOR
CLARIFIED SPENT LIQUOR
ASH-CaSO₃·2H₂O CLARIFIER
MIXER
AGITATED CRYSTALLIZER
ZINC SULFITE SLURRY
WATER
SODA ASH
ZnSO₃·2½H₂O FILTER
LIMING TANK
LIME CaO
ZnO
HOT EXHAUST GAS
AIR
FUEL OIL
DRYER
GASIFIER
ZnO
CALCINER
ZnSO₃·2½H₂O
HAMMER MILL
CYCLONE
BLOWER
WET EXHAUST
ZnSO₃·2½H₂O (FINES)
BLOWER
ZnO FINES
CYCLONE
CaSO₄ THICKENER
SO₂ FROM COOLERS
SO₂ LIQUEFACTION PLANT
LIQUID SO₂
CaSO₄ FILTER
WATER
WET CaSO₄ AND ASH

Fig. 3. Regenerative sodium sulfite process for the removal of sulfur dioxide.

Ammoniacal Liquor Process

The reaction of ammonia and sulfur dioxide in flue gas results in the formation principally of ammonium sulfate, with small amounts of the sulfite, bisulfite, and thiosulfate formed. The principal reactions are:

$$2NH_3 + H_2O + SO_2 \rightarrow (NH_4)_2SO_3 \quad (1)$$

$$NH_3 + H_2O + SO_2 \rightarrow NH_4(HSO_2) \quad (2)$$

$$(NH_4)_2SO_3 + \tfrac{1}{2}\,O_2 \rightarrow (NH_4)_2SO_4 \quad (3)$$

Absorption towers are similar to those used in the limestone process, and the design of these towers was based upon the information given by Rees of the British Electricity Authority.(2) As shown in Fig. 2, 2 stages of scrubbing are provided to prevent excessive loss of ammonia, the second stage operating with a more dilute solution than the first. A bleed stream of spent solution from the absorbers is processed in the product recovery system. The major portion is recycled to the absorber after the required amount of fresh ammonia has been added. The bleed stream is treated with sulfuric acid in an autoclave at 200 lb./in.^{2} pressure and about 360°F. About 90% of the sulfur dioxide removed is recovered in the form of ammonium sulfate and the remaining 10% as free sulfur. After the ammonium sulfate solution leaves the autoclave, it flows to evaporators and crystallizers, where solid ammonium sulfate is recovered.

Regenerative Sodium Sulfite Process

The characteristic features of the sodium sulfite process follow:

(1) Sulfur dioxide is removed from the flue gas by countercurrent scrubbing with a solution containing sodium sulfite and bisulfite. Sodium bisulfite is the major product, but some sulfate ion is formed by reaction of sodium sulfite with oxygen in the flue gas.

(2) A slurry of calcium sulfite is added to the spent solution to remove the sulfate ion by the formation of insoluble calcium sulfate.

(3) After the spent solution is desulfated, it is treated with zinc oxide to form a solution of sodium sulfite and a precipitate of zinc sulfite. The sodium sulfite is returned to the absorber, while the zinc sulfite is filtered off, dried, and calcined to recover sulfur dioxide and regenerate zinc oxide for reuse. If sulfate ions were present in the spent solution, losses of zinc would occur by the formation of soluble zinc sulfate.

The various steps of the process are illustrated by the flowsheet given as Fig. 3, and its operation briefly described as follows: absorption of sulfur dioxide occurs in the scrubber by means of the following reaction:

$$H_2O + SO_2 + Na_2SO_3 \rightarrow 2NaHSO_3.$$

The sodium bisulfite content of the spent liquor depends upon the amount of sulfur dioxide absorbed. A slurry containing calcium sulfite is added to the spent liquor in a clarifier. The spent liquor contains a small amount of fly ash, most of which is removed by settling in the ash clarifier. Underflow from the clarifier, consisting of a slurry of ash and calcium sulfite and sulfate, flows to a gasifier, where sulfur dioxide is added to convert the calcium sulfite to soluble calcium bisulfite,

$$CaSO_3 + H_2O + SO_2 \rightarrow Ca(HSO_3)_2.$$

Ash and calcium sulfate are filtered from the solution of calcium bisul-

TABLE I

Nonregenerative Limestone Process Capital Costs

	SO$_2$ content of raw gas, vol.—%		
	0.083	0.30	
	90% removal	90% removal	70% removal
Major equipment installed	$ 537,250	$ 649,450	$ 569,450
Piping	268,500	325,000	285,000
Instruments	18,900	22,800	20,000
Electrical	18,900	22,800	20,000
Mechanical handling	10,800	13,000	11,400
Yard improvements	37,600	45,500	39,900
Buildings	112,200	136,800	120,000
Miscellaneous	40,300	48,600	42,600
General utilities and facilities	40,300	48,600	42,600
Physical Plant Cost	$1,084,750	$1,312,550	$1,150,900
Engineering and construction[a]	282,100	341,100	299,400
Contingency	130,200	157,500	138,100
Fixed Capital	$1,497,050	$1,811,100	$1,588,400
Working capital	149,700	181,100	158,800
Total Investment	$1,646,750	$1,992,200	$1,747,200

(a) Includes field indirect costs, engineering, overhead and purchasing, and contractors' fee.

fite, which is treated with lime to form calcium sulfite for another cycle of desulfation.

Clarified spent liquor goes to a mixer, where the proper amount of zinc oxide is fed. While in the mixer, zinc oxide is dispersed in the solution, and then the insoluble zinc sulfite begins to form. Crystallization of hydrated zinc sulfite is completed in an agitated crystallizer by the reaction

$$ZnO + 2\ NaHSO_3 + 1.5\ H_2O \rightarrow ZnSO_3.2.5\ H_2O + Na_2SO_3.$$

The hydrate of zinc sulfite is filtered, dried, milled, and calcined and finally returned to the mixer as zinc oxide. The filtrate separated from the zinc sulfite slurry constitutes the regenerated liquor and is pumped back to the absorber for further removal of sulfur dioxide.

Hot gaseous sulfur dioxide and water vapor leave the calciner and are cooled in the liquefaction plant. The condensed water is returned to the agitated crystallizer. Part of the cooled sulfur dioxide gas is sent to the gasifier, and the rest is liquefied for shipment.

This process is essentially self-contained. Makeup chemicals are required primarily as a result of sulfite oxidation, spray losses at the scrubber, and dust losses from the calciner and drier. The presence of hydrogen chloride or oxides of nitrogen in the flue gas causes loss of zinc and other reagents by formation of soluble chlorides and nitrates. Lime input is stoichiometrically equal to the waste calcium sulfate; zinc oxide is used to replace the dust losses; sodium carbonate replaces the salts lost in the absorber spray.

Cost Estimates

Capital Costs

Capital costs were obtained by estimating the installed costs of the major equipment and assigning to each factors for piping, instrumentation, and other items based upon whether the material being processed was solid or fluid. Installed costs of the major items were estimated from the data of Aries and Newton,(3) Chilton,(4) and Nelson.(5) Factors of 1.3 and 1.1 were used to translate costs from 1949 and 1954, respectively, to 1956. The following information was used as a basis for estimating the capital costs: The general design basis, flowsheets, material balances, heat and energy balances, utility requirements, equipment lists and specifications, and a general layout of the units. Estimates based on these factors are considered to range from plus or minus 20% of the true cost.(6) However, since the same general assumptions were used for cost estimation for each of the 3 processes, it is believed that comparative error among the estimates is within plus or minus 5%.

TABLE II

Ammoniacal Liquid Process—Capital Costs

	SO₂ content of raw gas, vol.—%		
	0.083	0.30	
	90% removal	90% removal	70% removal
Major equipment installed	$1,066,390	$1,637,240	$1,342,700
Piping	501,200	769,000	630,000
Instruments	37,325	57,300	47,000
Electrical	37,325	57,300	47,000
Mechanical handling	21,330	32,800	26,900
Yard improvements	74,650	114,800	94,100
Buildings	223,940	343,800	282,000
Miscellaneous	79,900	122,800	100,900
General utilities and facilities	79,900	122,800	100,900
Physical Plant Cost	$2,121,960	$3,257,800	$2,671,500
Engineering and construction(a)	551,700	847,100	694,600
Contingency	254,600	390,900	320,600
Fixed Capital	$2,928,300	$4,495,800	$3,686,700
Working capital	292,800	449,600	368,700
Total Investment	$3,221,100	$4,945,400	$4,055,400

(a) Includes field indirect costs, engineering, overhead and purchasing, and contractors' fee.

The capital costs for the 3 processes are shown in Tables I, II, and III for the various cases of removal. The investment costs are lowest for the limestone process, ranging from $1,646,750 to $1,992,200, and are highest for the ammonia process, varying from $3,221,100 to $4,945,400. Those of the sodium sulfite process are intermediate and are lower than those of the ammonia process because only 1 stage of absorption is required. No byproduct recovery system is required for the limestone process, and accordingly its capital costs are less than those of the other processes. The plant investment of $1,646,750 for purification of the gas of low sulfur dioxide concentration by the limestone process can be compared with an estimate of £165,900 ($795,000) made by the British in 1932.(7) Since plant costs have risen

TABLE III

Sodium Sulfite Process—Capital Costs

	SO₂ content of raw gas, vol.—%		
	0.083	0.30	
	90% removal	90% removal	70% removal
Major equipment installed	$ 830,410	$1,060,090	$ 897,980
Piping	348,770	445,240	377,150
Instruments	29,060	37,100	31,430
Electrical	29,060	37,100	31,430
Yard improvement	58,130	74,210	62,860
Building	174,380	222,620	188,580
Insulation	8,300	10,600	8,980
Miscellaneous	62,300	79,500	68,100
General utilities and facilities	62,300	79,500	68,100
Physical Plant Cost	$1,602,710	$2,045,960	$1,734,610
Engineering and construction(a)	416,750	532,000	451,000
Contingency	192,300	245,500	208,100
Fixed Capital	$2,211,760	$2,823,460	$2,393,700
Working capital	221,200	282,300	239,400
Total Investment	$2,433,000	$3,105,800	$2,633,100

(a) Includes field indirect costs, engineering, overhead and purchasing, and contractors' fee.

TABLE IV
Utility and Chemical Requirements and Yield[(a)] of Byproducts

	Limestone process			NH_3 process			Sodium sulfite process		
SO_2 content of flue gas, vol.—%	0.083	0.30	0.30	0.083	0.30	0.30	0.083	0.30	0.30
Removal, %	90	90	70	90	90	70	90	90	70
Steam, lb./hr.	0	0	0	16,000	58,000	45,200	4,430	27,300	21,300
Water, gal./hr., fresh	9,760	11,160	9,130	13,020	23,970	18,670	19,200	75,900	59,100
Power, kw.-hr.	795	936	735	1,380	1,465	1,150	325	419	330
Fuel oil, gal./hr.	0	0	0	0	0	0	184	433	338
Chemicals, lb./hr.									
Limestone (95% $CaCO_3$)	4,400	15,900	12,400	—	—	—	—	—	—
Anhydrous NH_3	—	—	—	1,284	4,620	3,600	—	—	—
20% Oleum	—	—	—	262	945	735	—	—	—
Na_2CO_3	—	—	—	—	—	—	309	309	241
ZnO	—	—	—	—	—	—	29.7	70.0	63.1
Lime	—	—	—	—	—	—	1170	1170	913
Yield of byproducts, tons/day									
Ammonium sulfate	—	—	—	59.7	215.5	167.8	—	—	—
Sulfur	—	—	—	4.63	16.7	13.0	—	—	—
Sulfur dioxide	—	—	—	—	—	—	16.1	99.6	77.9

(a) Quantities for treating 20,000,000 SCFH flue gas.

2- to 3-fold in that time, the present-day equivalent might be approximated at about $2,000,000.

Operating Costs

Annual operating costs of the 3 processes were computed from the utility and chemical requirements shown in Table IV, the estimated labor requirements, and the capital costs. Yields of byproducts also are shown in Table IV.

Annual operating costs of the 3 processes are listed in Tables V, VI, and VII. Included in the direct costs are utilities and chemicals consumed, direct labor, plant maintenance, payroll overhead (18.5% of payroll), and operating supplies (15% of maintenance). Indirect costs are charged at 50% of operating labor, direct supervision, plant maintenance, and operating supplies. Fixed costs consist of taxes and insurance at 2% and depreciation at 5% of the fixed capital.

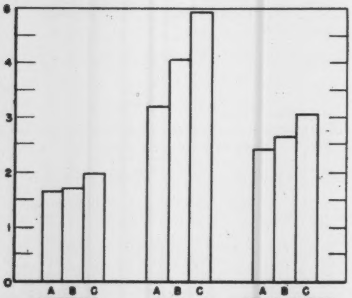

Fig. 4. Capital cost of SO_2—removal processes.
Case A—90% removal from gas of 0.083% SO_2 content.
Case B—70% " " " " 0.30
Case C—90% " " " "

The following charges have been made for utilities and chemicals:

Power
— $ 0.0055/kw. hr.
Fresh water
— .10/1000 gal.
Circulating water
— .03/1000 gal.
Steam
— .37/1000 lb.
Fuel oil
— .073/gal.
Limestone
— 6.00/ton delivered
Anhydrous ammonia
— 100.00
Oleum
— 35.00
Sodium carbonate ($Na_2CO_3.H_2O$)
— 63.40
Lime
— 15.00
Zinc oxide
— 305.40

TABLE V
Nonregenerative Limestone Process—Annual Operating Costs (330 days' operation)

	SO_2 content of raw gas, vol.—%		
	0.083	0.30	
	90% removal	70% removal	90% removal
Direct costs			
(a) Raw materials			
Power	$ 34,600	$ 40,800	$ 32,000
Fresh water	7,750	8,850	7,250
Limestone	104,050	378,000	295,000
	$147,050	$427,650	$334,250
(b) Direct labor 4 men/shift at $2.25/hr./man plus supervision	90,700	90,700	90,700
(c) Plant maintenance			
Labor	62,400	72,000	67,100
Materials	36,800	40,900	38,100
(d) Payroll overhead	28,400	30,100	29,200
(e) Operating supplies	14,900	16,900	15,800
Total direct costs	$380,250	$678,200	$575,150
Indirect costs	102,500	110,300	105,900
Fixed costs			
Taxes and insurance	29,800	36,200	34,950
Depreciation	74,800	90,500	87,000
Total operating costs	$587,500	$915,200	$803.000
Cost: $/ton coal consumed	1.24	1.93	1.69
mills/kw. hr.	0.62	0.87	0.85

TABLE VI

Ammoniacal Liquid Process—Annual Operating Costs (330 days' operation)

	SO$_2$ content of raw gas, vol.—%		
	0.083	0.30	
	90% removal	90% removal	70% removal
Direct costs			
(a) Raw materials			
Steam	$ 46,800	$ 170,200	$ 132,800
Power	60,100	63,900	50,000
Fresh water	10,320	18,990	14,780
Circulated water	7,690	27,700	21,600
Anhydrous ammonia liquor	509,000	1,830,000	1,425,000
Oleum	36,300	130,800	101,800
	$ 670,210	$2,241,590	$1,745,980
(b) Direct labor 5 men/shift at $2.25/hr./man plus supervision	113,300	113,300	113,300
(c) Plant maintenance			
Labor	97,420	101,710	99,500
Materials	97,420	101,710	99,500
(d) Payroll overhead	39,000	39,800	39,300
(e) Operating supplies	29,450	31,200	29,800
Total direct costs	$1,046,800	$2,629,310	$2,127,380
Indirect costs	168,800	174,000	171,100
Fixed costs			
Taxes and insurance	58,500	89,900	73,700
Depreciation	146,200	214,600	184,500
Total operating costs	$1,420,300	$3,107,800	$2,556,700
Cost: $/ton coal consumed	2.99	6.54	5.38
mills/kw. hr.	1.50	3.27	2.69

The operating costs of $1.24 to $1.93/ton of coal consumed for the limestone process are the lowest in all 3 cases if no credit for byproducts is allowed for the ammonia and sodium sulfite processes. A comparison summarizing the operating and investment costs is shown in Table VIII. This comparison is facilitated by the use of Fig. 4 and 5, in which the capital and operating costs of the processes are illustrated by bar graphs. If the ammonium sulfate and sulfur produced in the ammonia process can be credited at their market prices at the end of 1956 of $32.00 and $28.00/ton, respectively (Table IX), the operating costs of the ammonia process become the lowest for purification of the gas containing 0.30% sulfur dioxide. The operating costs of the sodium sulfite process for purification of the gas of high sulfur dioxide content approach those of the limestone process when the byproduct sulfur dioxide is credited at $14.00/ton. The market price of liquefied sulfur dioxide is about $90.00/ton, because of the extremely limited demand for this material, but the sulfur dioxide has been credited at a value equivalent to sulfur at $28.00/ton. As shown in Table IX, the highest byproduct credit can be obtained if sulfuric acid is recovered as the byproduct.

Extreme caution must be used in allowance for byproducts, especially in the case of ammonium sulfate. The total quantity of ammonium sulfate produced from ammonia in 1955 (1,131,106 tons)[8] would be obtained from only 16 power plants of 120,000 kw. capacity in which 90% of the sulfur dioxide was removed from a flue gas containing 0.30% of this material. On the other hand, allowance of byproduct credit for sulfur and sulfur dioxide is less speculative. Approximately 90% of the sulfur produced or recovered in various forms eventually is converted to sulfurous and sulfuric acid, with sulfur dioxide the intermediate product.[9] The sulfur dioxide recovered from the flue gas of a 120,000 kw. power plant would be equivalent to only one-three hundredth of the 1955 consumption of 15,800,000 tons of sulfuric acid.

General Considerations

In general, the capital requirement for a power plant burning coal would be increased 10 to 20% by the addition of scrubbing facilities. The operating costs/ton of coal consumed

TABLE VII

Sodium Sulfite Process—Annual Operating Costs (330 days' operation)

	SO$_2$ content of raw gas, vol.—%		
	0.083	0.30	
	90% removal	90% removal	70% removal
Direct costs			
(a) Raw materials			
Power	$ 17,750	$ 22,850	$ 18,000
Fresh water	19,000	75,000	58,500
Steam	16,000	98,700	77,000
Fuel oil	133,000	302,700	238,750
Sodium carbonate	90,900	90,900	70,900
Lime	69,400	69,400	54,100
Zinc oxide	35,900	84,700	76,300
	$ 381,950	$ 744,250	$ 593,550
(b) Direct labor 5 men/shift at $2.25/hr./man plus supervision	113,300	113,300	113,300
(c) Plant maintenance			
Labor	77,500	99,000	84,000
Materials	77,500	99,000	84,000
(d) Payroll overhead	35,200	39,300	36,500
(e) Operating supplies	23,200	29,700	25,200
Total direct costs	$ 708,650	$1,124,550	$ 936,550
Indirect costs	145,800	170,500	153,000
Fixed charges			
Taxes and insurance	44,200	56,500	47,900
Depreciation	110,800	141,200	120,000
Total operating costs	$1,009,400	$1,492,800	$1,257,500
Cost: $/ton coal consumed	2.13	3.15	2.65
mills/kw. hr.	1.07	1.58	1.33
$/ton of liquid SO$_2$ produced.	185.5	42.3	44.3

TABLE VIII
Summary of Costs of Scrubbing SO_2 from Flue Gas[a] of Power Plant of 120,000-Kw. Capacity

	SO₂ content of flue gas before scrubbing, vol.—%					
	0.083		0.30			
	90% removal		90% removal		70% removal	
***Total investment*[b]**						
Limestone process	$1,646,750		$1,992,200		$1,747,200	
Ammonia process	3,221,100		4,945,400		4,055,400	
Sodium sulfite process	2,433,000		3,105,800		2,633,100	
***Annual operating costs*[c]**	$/ton coal consumed					
	No credit for products	Credit for[d] products	No credit for products	Credit for[d] products	No credit for products	Credit for[d] products
Limestone process	1.24	—	1.93	—	1.69	—
Ammonia process[e]	2.99	1.62	6.54	1.43	5.38	1.41
Sodium sulfite process	2.10	1.97	3.21	2.17	2.75	1.91

(a) 475,000 tons/year coal consumed; sulfur content of 1.5 and 5%, respeotively.
(b) Including working capital at 10% of fixed capital.
(c) No provision for return or interest on investment.
(d) Ammonium sulfate at $32.00/ton; sulfur at $28.00/ton; SO_2 at $14.00/ton. (Sulfuric acid equivalent price.)
(e) Anhydrous ammonia charged at 100.00/ton delivered.

vary from about $1.25 to $2.00, allowing credit for products and for the ammonia and sodium sulfite processes would be appreciably higher, with no byproduct credit allowed. This amounts to operating costs from about 0.6 to over 1 mill/kw. hr. of power generated, without charge on the capital investment. Actually, the cost of the coal consumed to generate power amounts to only 2 to 3 mills/kw. hr., with the cost of coal in the $4.00 to $6.00/ton price range.

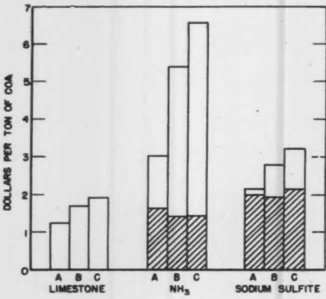

Fig. 5. Operating cost of SO_2 removal processes. Top of shaded areas show net cost after allowing byproduct credit.
Case A—90% removal from gas of 0.083% SO_2 content.
Case B—70% " " " " 0.30
Case C—90% " " " "

No allowance has been made in these estimates to provide for capital charges. These will vary, depending upon the method by which the plant is financed. The capital charges for the various plants at rates of 6, 9, and 12% are shown in Table X. For a charge of 6%, the cost of sulfur dioxide removal would be increased from $0.21 to $0.62/ton of coal above the costs shown in Table VIII.

Although the costs of these purification processes reflect an appreciable increment/ton of coal consumed or power generated, they are consistent with the costs to be expected for the type of chemical operations involved. Undoubtedly improved process techniques can effect significant reduction in the cost of removing sulfur dioxide from flue gases.

Purification processes operating at normal flue gas temperatures would have advantages both costwise and from a technical point of view. After purification, the hot gases would be discharged in the usual fashion and disperse readily, whereas, when the flue gas is cooled, additional power is required to discharge it, and there is the possibility of rapid settling and localized pollution by the residual sulfur dioxide. Pollution due to this

TABLE IX
Market Prices of Sulfur Products, 1956[a]

Product	Dollars/ton	Dollars/ton sulfur equivalent
Sulfur	28.00	28.00
Sulfuric acid (100%)	23.50	71.90 (3.06 tons)
Ammonium sulfate	32.00	24.70 (3.94 tons)[c]
Sulfur dioxide, gas	14.00[b]	28.00 (2 tons)

(a) *Chemical and Engineering News*, Prices, 4th quarter, 1956.
(b) Computed as sulfur equivalent.
(c) Corrected for 1.015 tons of ammonia required at $100.00/ton delviered.

TABLE X
Capital Charge on Total Investment ($/ton coal consumed)

	Capital charge, %		
	6	9	12
Limestone process:			
0.083% SO_2 in gas	0.21	0.31	0.42
.30% SO_2 in gas			
90% removal	.25	.38	.50
70% removal	.22	.33	.44
Ammoniacal liquid process:			
0.083% SO_2 in gas	.41	.61	.81
.30% SO_2 in gas			
90% removal	.62	.94	1.25
70% removal	.51	.77	1.03
Sodium sulfite process:			
0.083% SO_2 in gas	.31	.46	.62
.30% SO_2 in gas			
90% removal	.39	.59	.78
70% removal	.33	.50	.67

cause has actually occurred at a power station in England where liquid scrubbing was employed.$^{(1)}$

Other desirable features to achieve cost reductions are:

(1) Use of absorbents that are readily reactivated for reuse with minimum replacement.

(2) Recovery of the sulfur dioxide in a convenient form for sulfuric acid production rather than in some less valuable form or as a waste product for which no credit can be obtained.

(3) Development of a simple process scheme for both purification and byproduct recovery to reduce capital costs.

However, regardless of the amount of cost reduction achieved by improved processes, necessarily there will be additional capital outlay and operating costs to remove sulfur dioxide from flue gases. These costs will have to be added to the cost of power generation and may be justified by the advantages of cleaner air.

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The Use of Sticky Paper In An Air Pollution Monitoring Program*

CHARLES W. GRUBER and GEORGE A. JUTZE
City of Cincinnati
Cincinnati, Ohio

Large particles are a very important part of the Cincinnati Air Pollution complex and are the objects of many nuisance complaints to the Cincinnati Bureau of Air Pollution Control. For example, causes of citizen protests are found in the grit on the porch, the fly ash on the nice new cream colored auto of the night watchman, or the specks on the important letter freshly typed by the boss's secretary. Complaints reflect the subjective reaction of people to varying degrees of particle deposit based on their individual temperament and what they have been accustomed to, and is generally unrelated to the quantity of fall reported in the monthly dust fall report. One would expect this because of the wide variation in levels from local sources. For purposes of this paper large particles are considered to range upward from 5μ, which size can be readily observed as individual particles with well lighted magnification of about 14x.

Our long experience with dust fall measurement by the jar method has taught us the shortcomings of the dust fall station in an effort to locate the offender in a complaint situation caused by large particles or grit. A dust jar will give no indication of the direction or the source of the material collected.

The early development of the Directional Dust Fall Collector at Battelle Memorial Institute by H. P. Munger and his associates was watched with keen interest. However, the complexity of the device led to a rather high cost instrument when it was produced commercially. This instrument may be suitable for a single sample station, but the need for a multiplicity of sampling stations in connection with large particle study indicated that a more simplified technique was desirable.

The results of dust fall are generally reported as a weight of fall/unit of area. The weight of fall is not the best indication of the nuisance effect of large particle fallout because of the very wide range of particle size. The number of particles collected is a far more important factor in the process of evaluating a given situation.

There is nothing new or original about the use of sticky paper in collecting particle fallout for study. Much use has been made of such materials as greased aluminum foil or adhesive materials mounted horizontally as flat surfaces on which the particles are trapped as they fall to the ground from high places. The usual evaluation is by weight, before and after exposure.

Having before us the need for a direction indication from which the particles originate and a better means of evaluation than mass rate of fall. attention was given to the possibility of using an adhesive surface placed vertically with the catch being evaluated by visual means. Since the nuisance of large particles is associated largely with particles which are dark colored, mostly black, the use of white adhesive paper was a logical choice. So perhaps then, the most important contribution of the Cincinnati method is the use of the vertical surface for direction indication and the determination of an estimated count of the particle catch by visual reference to a set of *standards* which have been carefully counted. An instrument was then constructed

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* Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

TABLE I
1955 Comparative Sticky Paper Surveys

		Particles/in.^{2}								Tot. part./ week/8 in.^{2} all direct.	Top fall part. /in.^{2}	Date
		N	NE	E	SE	S	SW	W	NW			
Downtown	Dirtiest Week	21000	21000	18000	18000	18000	18000	21000	21000	156000	21000	2/28-3/7/56
	Cleanest Week	4400	4400	6000	15000	8700	12000	15000	12000	77700	15000	3/14-3/21/56
	Average Week	7800	9700	14000	15000	13000	15000	17000	11000	103000	19000	Avg.
Residential	Dirtiest Week	2900	1800	2900	18000	18000	9000	2900	2900	52900	6400	2/9-2/16/56
	Cleanest Week	1800	1800	1800	2900	4400	1800	1800	1800	17900	1800	7/26-8/2
	Average Week	3000	2500	2300	4700	4800	3600	2100	1900	25100	4700	Avg.

to rapidly evaluate the test catch according to 8 directions of the compass as well as the vertical fallout and the results recorded by a count number ranging from 1 to 9. Thus, the result of the particle catch is recorded as a number which in turn has been calibrated to a *psi. (of collecting surface)* value.

As often happens the complicated device is first conceived and leads the way to simple solution. One of the early instruments constructed and then discarded was a circle of adhesive paper wrapped around the outside of an 8 in. dia. fruit cake tin plus a flat disc faced upward. This holder was stationary. Around this holder was a rotating shield in which was a 2 x 2 window cut in the shield in the vertical side and one in the top. To the shield was fastened a wind vane and the unit set out to rotate with the wind and expose only the down wind face while the rest of the *adhesive strip* was protected. The results were not in any way commensurate with the effort and little directional pattern was evident on the *catch*. However, when the complicated shield was removed and the circular adhesive paper exposed the results were quite directional. Then a few strips of the adhesive paper were wrapped around light poles and from this point the circular jar methods for holding the sticky paper in the field were developed. The use of the jar tied nicely with the construction of the *particle comparator*. A more detailed description of the technique and instrumentation follows.

The paper used is a self adhesive label paper. One hundred sheets, 25½ x 20 in. may be purchased for $22.50. Jars are a standard item at any supply house, being 2½ in. in diam. and 3½ in. deep. The screw top is riveted to the end of a ½ in. wood bracket which is 18 in. in length and easily attached to any suitable support. The usual support used in our program is a utility pole mounted about 10 ft. off the ground.

The visual comparator consists of a cylinder, 4½ in. in diam., attached to a slotted gear indicator by means of a drive shaft. The gear contains 8 slots, allowing for the 8 points of the compass. The standards are mounted on the cylinder, directly under an observation slot, by means of black plastic tape. The cylinder is rotated manually as each point of the compass is read. The standards and samples are then viewed through a fluorescent, illuminated magnifier of 4 power magnification with rigid 6 in. arms and a portable base. The comparator was designed and constructed by the author. The viewer is a standard illuminated inspection glass.

The standards are prepared by random scattering of typical particulate matter on sticky paper. This may be accomplished by use of an air spray or by physical scattering. These *catches* are then sprayed with clear plastic preservative, and, after drying, portions are selected which visually approximate the desired particle count. These portions are cut into 1 in. squares and then counted under 14x magnification. By necessity, a trial and error method of selection must be used until the desired standards are found. They are then assigned an intensity code number.

TABLE II
Variation of the Shaded Jar From the Average of the Other Three for the Same Time Period

Date	North	East	South	West	Average variations in code units
11/27-12/4	−⅔	−1	−⅓	−1⅔	−9/10
12/4 -12/11	−⅓	+⅓	−⅔	0	−⅕
12/11-12/18	−1	−⅓	−1	−⅓	−7/10
12/18-12/26	0	−⅓	+⅓	−⅔	−⅕
12/26-1/1/57	−⅔	+⅓	+⅔	+⅓	+⅕
1/1 -1/8	−⅔	−⅓	+1⅓	−⅔	−1/10
1/8 -1/15	−⅓	0	−⅓	−⅓	−¼
1/15-1/21	0	−1	−⅔	−1	−7/10
1/21-1/28	−⅓	−⅓	0	+1⅔	+¼
1/28-2/6	0	−1	+⅓	+⅓	−1/10
2/6- 2/11	−⅓	0	0	0	−1/10
2/11-2/18	−1	+⅔	−2	+⅓	−½
2/25-3/4	0	−⅓	−⅔	−1	−½
3/4 -3/11	+⅔	−⅓	−⅔	−1	−⅓
3/11-3/18	−⅔	−1⅓	0	+1⅓	−⅕

Average Variation = —¼ Particle Catch/evaluation Number.

In our program, these code numbers are used as follows:

1 — 1250 pp./in.^{2}
2 — 2500 ”
3 — 3750 ” Large and small
4 — 7500 ” ” ” ”
5 — 10000 ” ” ” ”
6 — 17500 ” Large and small
7 — 22500 ”
8 — 30000 ”
9 — 45000 ”

In the range of 3750 to 17500 particles/in.^{2} that is, the transition period from a small to a larger type of particle, 2 standards are prepared for each intensity number. We have found that in our particular case, we may catch small and large particulates or a mixture of both, depending on influencing conditions. Thus, a standard composed of small particles and one with significantly larger particles are mounted side by side on the comparator to aid in a more true evaluation of the sample.

The selection of a sampling site should be a matter of good judgment. It is suggested, however, that the general specifications outlined in the Air Pollution Measurement Committee Report of the APCA on dust fall measurement stations would apply in a majority of cases. The jars set out in our program are mounted in 2 ways. The previously described bracket is attached to utility poles while in many cases we use a 6 ft. metal pole cemented into a discarded auto battery box. The screw cap is then soldered to the top of the pole and this becomes a very suitable mount for mobile operations. In the routine air monitoring program, an exposure period is 1 wk., but in our spot studies, the period is determined by the situation.

When the sampling period has been completed, the samples are returned to the laboratory in a dust-free carrying case and immediately evaluated. The jars are placed on the comparator and the eight directional and top catch estimates are made. If the sample contains any unusual particulate or if any of the catch necessitates identification, the paper is sprayed with plastic, the desired section cut out and observed under the microscope using direct light.

The intensity numbers for the 8 side readings and the top-fall reading are then received on a standard data sheet. This record sheet is nothing more than a form showing date, exposure period, 8 directional and 1 top-fall columns and final space for remarks. By use of this type sheet, our data is presented both concisely and completely in a neat and efficient manner.

A good example of our method of reporting results may be illustrated by the 1955 yearly averages, including the cleanest and dirtiest periods for the year. They are shown in Table I.

In order to determine if a utility pole exhibited any *shading* influence on the bracket mounted sticky paper jar, a 15-wk. survey was undertaken. Four jars were mounted at the same level on a utility pole, with each bracket directed to one of the 4 major points of the compass. All 4 jars were oriented to the north as required by our sampling procedure. It is easily seen that any *shading* by the utility pole would be indicated on that jar which was located behind the pole in the path of any prevailing wind. Tables II and III indicate the result of the survey.

Examination of the data shows an average variation of the shaded jar from the average of the other 3 for the same time period of — ¼ particle catch number. This influence lies well within the accuracy of the method.

TABLE III
Four Selected Weeks From 15-Wk. Test
Showing Best and Worst Week Data

Date	Segment evaluated	N	E	S	W	Date	Segment evaluated	N	E	S	W
12/18/56 — 12/26/56	Range	0	2-3	3-4	3-4	2/6/57 — 2/11/57	Range	3-4	0	0	0
	Average Catch on 3 Open Segments	2	2⅓	3⅔	3⅔		Average Catch on 3 Open Segments	3⅓	2	3	3
	Catch on Segment of Shaded Jar	2	2	4	3		Catch on Segment of Shaded Jar	3	2	3	3
	Shaded Jar	s	w	n	e		Shaded Jar	s	w	n	e
2/11/57 — 2/18/57	Range	0	2-3	0	3-4	3/11/57 — 3/18/57	Range	3-4	3-5	0	5-7
	Average Catch on 3 Open Segments	4	2⅓	4	3⅔		Average Catch on 3 Open Segments	3⅔	4⅓	9	5⅔
	Catch on Segment of Shaded Jar	3	3	2	4		Catch on Segment of Shaded Jar	3	3	9	7
	Shaded Jar	s	w	n	e		Shaded Jar	s	w	n	e

Incinerator Testing and Test Results

A Written Discussion and the Author's Closure

Written Discussion

ROBERT L. DAUGHERTY
California Institute of Technology
Pasadena, Calif.

Mr. F. R. Rehm has presented a useful and valuable paper which should lead to a better understanding of this subject. But some comments are in order concerning his statements regarding 12% CO_2 as a standard rather than a 50% excess air basis. He states the following: A correction to a 50% excess air basis requires certain specific information and some assumptions to be made. The moisture content of the feed material must be determined and an ultimate analysis of the incinerator refuse material would be required. With the foregoing information he proposes that the theoretical air requirements be calculated and from this the weight of gases with 50% excess air can be determined. The Orsat analysis permits one to calculate the actual weight of gases/lb. of refuse and then all of this enables one to adjust the actual measured dust loading to a 50% excess air basis. He very properly states that all of this is involved and is impractical.

Fortunately all of these involved laboratory tests and calculations are unnecessary. It is just as easy to transform dust loading to any excess air basis as it is to calculate it at any percentage of carbon dioxide. In either case an Orsat analysis is all that is required. It is not necessary to know a single thing about the fuel or refuse being burned.

As an illustration suppose that all we have is an Orsat analysis and in a specific case it is:

$$\begin{aligned} CO_2 &= 13.75\% \\ CO &= 0.00 \\ O_2 &= 2.87 \\ N_2 &= 83.38 \\ \hline &\ 100.00\% \end{aligned}$$

The ratio

$$\frac{\text{air supplied}}{\text{air required}} = \frac{N_2}{N_2 - 3.78\,(O_2 - 0.5\,CO)} = 1.15$$

or 15% excess air is supplied. An alternate procedure is

$$\frac{100\,(O_2 - 0.5\,CO)}{0.264\,N_2 - (O_2 - 0.5\,CO)} = 15\%_{\text{excess air.}}$$

These formulas are accurate. The only assumption involved is that all of the nitrogen in the flue gas is from the air. But the amount of nitrogen in the fuel or refuse is so small in comparison that the error is negligible.

To prove the accuracy of the calculation the more involved calculations will now be presented for the corresponding fuel which is

$$\begin{aligned} C &= 0.853 \\ H_2 &= 0.113 \\ S &= 0.007 \\ N_2 &= 0.007 \\ O_2 &= 0.005 \\ \text{Water} &= 0.015 \\ \hline &\ 1.000 \text{ lb.} \end{aligned}$$

The air theoretically required/lb. of this fuel is 13.717 lb. For complete combustion with 15% excess air the products are:

$CO_2 = 3.128$ lb.
$H_2O = 1.017$
$H_2O = 0.015$
$SO_2 = 0.014$ from H_2 in fuel
$O_2 = 0.478$ from water in fuel
$N_2 = 12.112$
16.764 lb.

In the Orsat apparatus the reagent which absorbs and thus measures the CO_2 also absorbs SO_2 and hence the latter will appear in the Orsat analysis as so much CO_2. Thus the computed Orsat analysis for the dry flue gas will be:

$$\begin{aligned} CO_2 &= 13.725\% \text{ by volume} \\ O_2 &= 2.878 \\ N_2 &= 83.382 \\ \hline &\ 99.985 \end{aligned}$$

The slight discrepancy between this table and that previously given may be attributed to the fact that there is actually some nitrogen in the fuel, and also all calculations employ the conventional values of atomic weights to 2 significant figures only instead of the more precise 4 figure values.

The value of 12% CO_2 corresponds to about 50% excess air for bituminous coal or other substances having about the same ratio of carbon to hydrogen. For the fuel used in this example 12% CO_2 corresponds to about 30% excess air while 50% excess air will give about 10.4% CO_2.

If it were possible to have complete combustion with natural gas with no excess air the value of the CO_2 percentage would be only 11.75, and this is a theoretical maximum only. In practice the maximum possible value is only about 9 or 10% CO_2. For coke-oven gas the maximum theoretical value of CO_2 for no excess air is 9.7% and the maximum possible value in reality is about 8%. Hence it is obvious that 12% CO_2 as a standard can have no real physical meaning for such fuels.

On the other hand for 12% CO_2, coke will have about 77% excess air and blast-furnace gas about 320% excess air. Hence it is seen that any CO_2 percentage is a very poor criterion, when the aim is to fix a standard that will allow a reasonable amount of air, but prevent an evasion of a law by an excessive dilution of the flue gas. It is seen that this can be accomplished by specifying some specific value of the percentage of excess air, which can be applied to all fuels or combustibles, and a simple Orsat analysis is all that is required.

Author's Closure

F. R. REHM
County of Milwaukee
Milwaukee, Wisconsin

We wish to thank Mr. Robert L. Daugherty for his kind words and comments with respect to our paper on *Incinerator Testing and Test Results.* We are always glad to receive constructive suggestions with respect to shortening and simplifying the calculations involved in reporting exit flue gas dustloadings.

As the sample calculations used in Mr. Daugherty's comments involved the burning of a material which resembles fuel oil, as per the ultimate analysis and the resulting flue gas analysis, we have substituted a material which more nearly approaches a mixed incinerator refuse in analysis and have used the standard excess air formulae to check out its accuracy. Using the chemical formulation of Cellulose $(C_6H_{10}O_5)_n$, the attached table had been prepared by Mr. J. E. Brown for presentation at the Buffalo APCA Meeting.

From this table it is obvious that the excess air formulae as proposed are probably satisfactory for use in the calculation to a 50% excess air basis. The assumption used in the derivation of these formulae — that all nitrogen in the flue gas is from the air probably introduces negligible error. However, not enough actual ultimate analyses of *mixed incinerator refuse* are available to us to further comment on this point. Then too, the use of the nitrogen percentage figure in an Orsat analysis introduces additional chance for error in such a calculation. We are all cognizant that the % Nitrogen figure in a conventional Orsat analysis is not a positive determination but represents the *catch-all* quantity.

A number of times in our paper we refrained from discussing the merits or demerits of the dustloading limitations now in effect in various communities. In Los Angeles County, Rule 53b sets the dustloading limitation at: *0.4 gr./ft.*^{3} *of gas calculated to 12% of carbon dioxide* (CO_2) *at standard conditions.* In Milwaukee County, we, like many communities in the country, have adopted the recommended ASME limitation — 0.85 lb. dust/1000 lb. flue gas, adjusted to a 12% Co_2 basis, or to a 50% excess air basis. Mr. Daugherty has in-

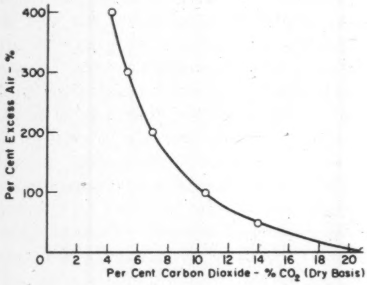
TABLE I

Combustion Data For Cellulose $(C_6H_{10}O_5)$—DRY

		Fuel			Air Supplied		Combustion Products					Ratio	Ratio	
		Mols.	At. Wt.	Wt. #	O_2	N_2	CO_2	H_2O	O_2	N_2	Total	Air/Fuel	C. Gas/ Fuel	Units
C		6	12.01	72.06#	6.	22.69	6.	—	—	22.69	28.69	4.782	4.782	Mols.
H_2		5	1.008	10.08#	(	(	—	(5.	—	—	5.00	2.392	2.890	Mols.
O_2		2.5	16.00	80.00#	(	(	—		—	—	—	—	—	Mols.
$C_6H_{10}O_5$		1	—	162.14#	6.	22.69	6.	5.00 *0.00	—	22.69	33.69 *28.69	28.69	33.69 *28.69	Total Mols.
Theoretical Combustion Air = 100%	100%	1			6.	22.69	6.	5.00 *0.00	—	22.69	33.69 *28.69	28.69	33.69 *28.69	Mols.
				1.00#	1.184	3.921	1.629	0.555 *0.000	—	3.921	6.105 *5.550	5.105	6.105 *5.550	Lbs.
							17.81 *20.91	14.84 *0.	— —	67.35 *79.09	100.00 *100.00	—	—	% Vol.
	150%	1			9.	34.04	6.	5.00 *0.00	3.	34.04	48.04 *43.04	43.04	48.04 *43.04	Mols.
				1.00#	1.776	5.883	1.629	0.555 *0.000	.592	5.883	8.659 *8.104	7.659	8.659 *8.104	Lbs.
							12.49 *13.94	10.41	6.24 *6.97	70.86 *79.09	100.00 *100.00	—	—	% Vol.
	200%	1			12.	45.38	6.	5.00 *0.00	6.	45.38	62.38 *57.38	57.38	62.38 *57.38	Mols.
				1.00#	2.368	7.842	1.629	0.555 *0.000	1.184	7.842	11.210 *10.655	10.21	11.210 *10.655	Lbs.
							9.62 *10.46	8.01 *0.00	9.62 *10.46	72.75 *79.08	100.00 *100.00	—	—	% Vol.
	300%	1			18.	68.08	6.	5.00	12.	68.08	91.08 *86.08	86.08	91.08 *86.08	Mols.
				1.00#	3.552	11.766	1.629	0.555 *0.000	2.368	11.766	16.318 *15.763	15.318	16.318 *15.763	Lbs.
							6.59 *6.97	5.49 *0.00	13.17 *13.94	74.75 *79.09	100.00 *100.00	—	—	% Vol.
	400%	1			24.	90.76	6.	5.00 *0.00	18.	90.76	119.76 *114.76	114.76	119.76 *114.76	Mols.
				1.00#	4.736	15.684	1.629	0.555 *0.000	3.552	15.684	21.420 *20.865	20.42	21.420 *20.865	Lbs.
							5.01 *5.23	4.18 *0.00	15.03 *15.68	75.78 *79.09	100.00 *100.00	—	—	% Vol.
	500%	1			30.	113.45	6.	5.00 *0.00	24.	113.45	148.45 *143.45	143.45	148.45 *143.45	Mols.
				1.00#	5.920	19.605	1.629	0.555 *0.00	4.736	19.605	26.525 *25.970	25.525	26.525 *25.970	Lbs.
							4.04 *4.18	3.37 *0.00	16.16 *16.72	76.43 *79.09	100.00 *100.00	—	—	% Vol.

*** — Dry Basis**

dicated that some excess air basis is a more equitable limitation than using the 12% CO_2 basis, and cited some different fuels and the amount of excess air to yield a 12% CO_2 condition. In the burning of natural and coke-oven gas it is theoretically impossible to reach a 12% CO_2 exhaust gas condition, he rightfully points out. We are in agreement with Mr. Daugherty's remarks on this subject and believe that in general that an excess air basis is a more equitable basis for setting a dustloading limitation. For some processes where dust is evolved and combustion does, or does not occur, or is incidental to the process, we actually feel that a *Process Weight* limitation has considerable merit and is a more equitable method of setting a limitation. Such limitation, however, complicates rather than simplifies the field testing needs of an air pollution control group.



Combustion data for cellulose $[C_6H_{10}O_5]_n$ —dry per cent excess air vs. per cent carbon dioxide (dry basis).

In line with the attached table, we submit the following graph which shows the % Excess Air vs. % Carbon Dioxide (% CO_2) — Dry Basis for the burning of cellulose. The best data we have seen to date indicates that the main combustible portion of incinerator feed material — paper, wood, cardboard, plant material, *etc.* would not deviate materially from cellulose in chemical analysis. From this graph, one can note that a 50% excess air basis would be equivalent to a 13.94% CO_2 basis (Dry) — or that a 12% CO_2 basis (Dry) would be equivalent to a 70% excess air basis. This explains the relatively close results we reported when calculating incinerator dustloadings on a 12% CO_2, or a 50% excess air basis.

Multi-Cycle and Long Cycle Automatic Impinger Sampling

W. J. WHITSELL
Oregon Air Pollution Authority
Portland, Oregon

The following excerpts from the author's letter were at the request for further information concerning construction details of the unit by the editor.

. . . The impinger tube to which you refer is only in part a specially blown item. The center tube together with its orifice and impingement plate is a unit, having been taken directly from the standard impinger (Smith-Greenburg). It was purchased directly from Corning Glass Works. Our only specification was that it be as shown in the Corning catalog LP 36, page 98, cat. no. 404650 and 7½ in. overall length. The outer glass casing with the drain fitting and side arm were specially formed by a local glass blower, as was the spray trap. Since these latter pieces are not a part of the *standard* for impingement, the actual dimensions are dictated only by the need for total volume and depth of liquid, and the desire for compactness. They are relatively inexpensive to make because they are open at the top.

Construction of an automatic impinger of the materials and design referred to in the paper requires some work of a specialized nature. This precludes the actual construction of such a unit by a *well organized department* unless such department be equipped to work with heavy gauge stainless steel sheets and do some machinery of stainless steel parts. They could, as we did, let portions of the fabrication out to specialists. In our case, most of the fabrication of the case was done by Losli Sheet Metal Works,* specialists in stainless steel fabrication. The author did some minor fabrication and all of the assembly in our own workshop. The actual cost of the unit can only be expressed as approximately $150 plus 120 man-hr. of labor. I have turned working drawings over to Losli Sheet Metal Works. They have been granted the right to fabricate, assemble and sell the units . . .

One of the limitations of automatic samplers heretofore available has been the lack of flexibility in the selection and use of timing cycles. Thus, if an instrument were built to provide a sampling cycle of, say, 1 hr., this cycle could not be changed without replacement of certain essential parts, such as timing motors or cams. Sampling times which would be adequate for industrial hygiene work would be too short for the much lower concentrations ordinarily encountered in air pollution. Also, where a few min. of sampling time might suffice for 1 pollutant *(e.g.* sulfur dioxide), a sampling cycle of several hrs. might be necessary for another *(e.g.* hydrogen fluoride.)

Recognition of these complications together with personnel and budget limitations led the author to begin a search for suitable methods and components which might be incorporated in a functional yet relatively inexpensive sampling instrument.

The specific emergency facing the Oregon Air Pollution Authority's staff was the need for an automatic impinger to sample fluorides in connection with the investigation of emissions from aluminum reduction plants. Already large sums of money had been involved in court settlements and other costly actions were pending. The need for an independent, supplementing investigation by the Authority was clear, but the drain on its resources would be at the expense of other investigations unless new methods could be devised.

It was agreed by the staff that, insofar as possible, the following requirements should be met:

(1) Long period sampling in order to obtain enough pollutant (in this case fluorides) to permit ready laboratory analysis.
(2) A variety of sampling cycles with a high percentage of sampling time in each cycle; easy conversion from 1 cycle to another.
(3) Reliable component parts requiring a minimum of service and adjustment.
(4) High resistance to corrosion and weather.
(5) Control of liquid losses because of evaporation and mechanical break-off.
(6) High reservoir capacity for long unattended periods and large number of samples.
(7) Smallest size and weight consistent with required performance.

Many months were spent in a search of literature for materials and component parts which would satisfy the requirements. Many methods of timing, dispensing of liquids, and evaporation control were investigated and discarded before a combination of elements was finally selected.

The requirement of long period sampling with a variety of cycles was satisfied by using a 12-hr. Haydon timing motor to drive a program disk into which program pins could be inserted. This disk, with its pins, was designed and positioned so that it would operate switches for control of a pump and solenoid valves, and would rotate a table holding the receiving tubes. Thus, 1 program pin provides a 12-hr. cycle; 2 pins, 6-hr. cycles; 3 pins, 4-hr. cycles; 4 pins, 3-hr. cycles; 6 pins, 2-hr. cycles; and finally 12 pins for 1-hr. cycles. For the 6-hour cycle, actual sampling time (when pump is running) is about 92% of the cycle time.

Resistance to corrosion was obtained by the use of stainless steel and plastics. The top and control base are of stainless steel; the case and door of polyvinyl chloride sheet; and the rotating table of plexiglass. Supporting brackets, angle stiffeners, and machine screws are of stainless steel. Polyethylene tubing was selected because of its ready connection to nylon valve fittings and its high resistance to chemical attack.

Fig. 1.

Stainless steel solenoid valves made by General Controls were selected, 2 3-way and 2 straight-through valves being employed to accomplish the liquid control. **(Author's note:** *The selection of some controls was dictated as much by their availability at the time as by their satisfaction of our requirements. Identification of a manufacturer's product here does not necessarily constitute an indorsement of the product.)*

In the past, long period sampling had shown that mechanical break-off of tiny droplets of scrubbing solution could be significant, as evidenced by the liquid which accumulated in the spray trap just ahead of the pump. It is considered good practice to return this liquid to the original sample. A spray trap* was therefore designed and mounted so that any droplets trapped would be continuously returned to the original sample.

The problem of excessive evaporation was solved by providing for periodic releveling of the collecting solution in the impinger. This is accomplished by interrupting the sampling for 1 or 2 min. every hr. while the inter-connected impinger and the leveling reservoir permit the liquid levels to equalize. Design of the reservoir* precludes reverse flow from the impinger. When evaporation is great, replenishment is correspondingly more because of the greater difference in levels.

Large reservoir capacity was provided by mounting a large polyethylene cannister ($5\frac{1}{2}$ qt.) on top of the case. For long periods of unattended operation (1 week or more) in dry weather, the reservoir capacity can be doubled by placing another cannister alongside and connecting the 2 with a siphon. This arrangement permits refilling the reservoirs from the top without disturbing anything inside the case. It also reduces the chance of spillage inside the case.

Capacity of the rotating table is 40 tubes, space being provided by 2 concentric circles of holes, each circle with 20 holes. This arrangement permits a smaller cabinet size of less than 15 in. square.

The Oregon Air Pollution Authority's staff operated one of these automatic impingers (nicknamed *Autoimp)* for a period of $2\frac{1}{2}$ months at a station 85 miles from the home base

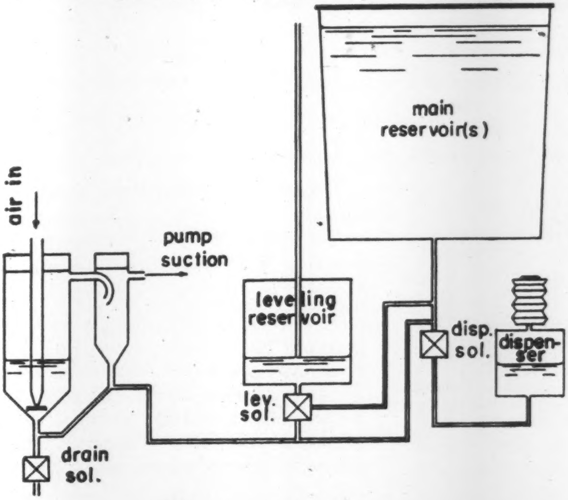


Fig. 2. Schematic flow diagram of automatic impinger.

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*Patent applied for.

of operations at Portland. The station was serviced only once a week, at which time the reservoirs were refilled, the rate of air flow checked, the samples removed from the instrument, and clean test tubes placed in position for the next week's sampling.

The total vol. of liquid deposited in the tubes can be adjusted by raising or lowering the leveling reservoir standpipe. The original vol. drawn into the impinger can be varied by adjusting the bellows to provide for greater or less expansion.

A typical sequence of events during a 6-hr. cycle would be as follows:

(1) Rest.
  - **a.** Drain solenoid open.
  - **b.** 3-way leveling solenoid connects leveling reservoir with main reservoir; leveling reservoir fills.
  - **c.** 3-way dispenser solenoid connects main reservoir with dispenser; bellows expand under pressure to permit entry of measured vol. of fresh liquid.
  - **d.** Pump still.

(2) Run.
  - **a.** Drain solenoid closed.
  - **b.** Leveling solenoid — no change.
  - **c.** 3-way solenoid connects dispenser with impinger; pump suction draws measured vol. of liquid into impinger; sampling proceeds.

(3) Level.
  - **a.** Drain solenoid closed.
  - **b.** 3-way leveling solenoid connects impinger with leveling reservoir, isolates both from main reservoir; fresh liquid flows from leveling reservoir to impinger until both are at same level.
  - **c.** Dispenser solenoid — no change.
  - **d.** Pump still.

(4) Run. Repeat "2".

(5) Level. Repeat "3".

(6) Steps "2" and "3" repeated alternately until end of sampling cycle.

(7) Rest. Repeat "1"; sample drains into receiving tube.

This treatment would not be complete without some mention of weather effects. The most dramatic effect, of course, is freezing. This will occur first in the impinger because of the rapid cooling produced by the inrushing cold air. This can be controlled by keeping a long sampling line inside a building or, in extreme cold, by wrapping the sampling tube with a heating tape. Timing motors and solenoid valves produce an appreciable amount of heat, but a special winter-time heater circuit controlled by a thermoswitch is ready to take over whenever the temperature in the case falls below 40°F.

The most troublesome element for equipment located out of doors is moisture. Particularly condensation, that old gremlin constantly on the prowl for unprotected devices, has probably been responsible for the destruction of more sampling equipment than any other single factor. It can develop short circuits, create shock hazard and accelerate corrosion. Either ventilation or heat can prevent condensation, but a combination of both is better; both have been installed in the *Autoimp* with good results.

This instrument has already proven to be a great time saver and a reliable addition to our equipment. Two others are now under construction and an additional unit will probably be built for the State's Occupational Health Division. It is hoped that this information will be of interest and aid to others in the field of air pollution and industrial hygiene who have been troubled by the problems associated with multicycle and long cycle air sampling.

An Automatic Programming Filter Sampler*†

GILBERT S. RAYNOR
Brookhaven National Laboratory
Upton, Long Island, New York

Introduction

In numerous studies involving air sampling, a need exists for a device that will take discrete samples periodically. A single sampler capable of fulfilling the diverse needs of various air sampling programs should meet the following criteria:

(1) It should be easy to construct, involve no precise machining and use mainly stock parts.
(2) It should have a wide selection of time periods.
(3) It should be simple and reliable in operation.
(4) It should be usable with various types and sizes of filters, at various flow rates and with any vacuum pump.
(5) It should be relatively inexpensive.

A sampler meeting these specifications has been developed by the writer for the Meteorology Group at the Brookhaven National Laboratory.

Numerous samplers, similar in purpose but different in design and operation, have been described, but none meet all of the above standards. Most, including those reported by Kuper, Foster and Bernstein (1950), Mansfield (1952), Wilson (1952), Hemeon, Sensebough and Haines (1952) and Lodge (1956), collect samples on filter paper in the form of strips or tapes which are moved either continuously or in periodic steps. Limitations of this method for certain applications are the lack of discreet samples when the tape is moved continuously, the possibility of loss from or addition to individual samples during the rewinding process, the problem of cutting and identifying each section of tape and the rather limited selection of timing cycles available. In addition, most of these samplers are apparently unable to use the rather fragile molecular filters.

The sampler reported by Hosey, Jones, Marsh and Gallagher (1954) uses 1 in. filters placed in holes near the edge of a revolving disk. This unit was designed for sampling radioactive materials, but could be modified for general air sampling by omission of the counting and recording sections. However, it is not commercially available and presents rather difficult machining and air seal problems. The Auto Sampler reported by Hall (1951) collects hourly samples on filter paper disks which are fed into place and removed periodically while the Owens Automatic Air Filter described in Shaw and Owens (1925) collects periodic samples in small circles near the edge of a large circular filter revolved in steps at 1 revolution/day. A sampler developed by Cryst, Gurney and Hansen (1955) has features in common with the one described in this paper, but uses a less versatile timing system. It's existence was not known when the present sampler was designed. A number of other filter samplers are described in the Encyclopedia of Instruments for Industrial Hygiene (1956). None, however, seem suitable for general application.

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* Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

† Research carried out under the auspices of the U. S. Atomic Energy Commission.

Design

The sampler described herein (Fig. 1) consists of 3 sections: (1) the sampling unit consisting of 10 solenoid operated valves connected to a common chamber through which air is drawn by a vacuum pump; (2) the basic timing unit which includes 2 readily interchangeable electric timing motors, a set of interchangeable cams and a stepping switch; (3) a program board between the other units which can multiply the length of any basic timing cycle, makes possible the collection of samples of unequal duration, provides for temporary suspension of sampling at the beginning of or at any point in the sampling cycle and provides for complete cessation of sampling and timing at any selected time.

Sampling Unit

The sampling unit (Fig. 2) includes 10 normally closed solenoid valves. The outlet side of each valve is inserted into the side of a common chamber, closed at one end and fitted with a single hose connection at the other. The intake side of each valve is fitted with a hose connection from which a plastic tube leads to a filter holder. The 10 filter holders are mounted in supports above the valves. Those currently in use are of the type previously described by Smith, Bartlett and Potts (1956). From the connection on the end of the brass tube, a plastic hose leads to the vacuum pump. Any type of vacuum pump, filter head or filter may be used, since none are integral parts of the sampler. A cover (not shown in the photographs) protects the filters from precipitation.

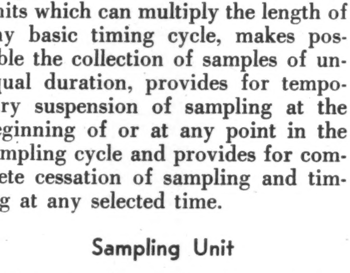

Fig. 1. Photograph of the complete Automatic Programming Filter Sampler.

TABLE I
Summary of Basic Time Periods

Notches on cam	Motor	
	1 RPH	1 RPD
1	60 Minutes	24 Hours
2	30 Minutes	12 Hours
3	20 Minutes	8 Hours
4	15 Minutes	6 Hours
6	10 Minutes	4 Hours
8	7.5 Minutes	3 Hours
12	5 Minutes	2 Hours

Measurement or control of the flow rate may be accomplished by means of a flow meter or other suitable instrument between the valves and the vacuum pump.

Timing Unit

The basic timing unit consists of an electric timing motor, a single cam-operated micro-switch and a 20 step, stepping-switch energized by a condenser discharge. In use, the stepping-switch is advanced 1 step each time the micro-switch lever is released by the timing cam. A one RPH or a one RPD motor used in conjunction with 1 of 7 cams, permits a selection from 14 basic time periods, (Table I). The timing circuit includes an outlet for the vacuum pump.

Program Unit

The program unit (Fig. 3), consists of a plug board mounted on the sampler end of the timing circuit chassis and 2 control relays.

Each socket of the plug board is wired to 1 of the 20 steps on the stepping switch. The ground lead from each solenoid is connected to the common point of the stepping switch. The other lead from each solenoid terminates in 2 or 3 plugs which may be inserted in any desired socket. If samples of uniform length are desired from each filter, for instance, a single plug from each solenoid is inserted in consecutive sockets on the board. If a double or triple length sample is desired from a filter, 2 or 3 plugs from the solenoid controlling that filter are inserted in appropriate sockets. Since only 20 steps are available, only 6 triple length or 10 double length samples can be taken.

The sampling delay control relay allows timing and stepping but not sampling to continue whenever the stepping switch is on a step connected to a delay plug. This feature permits starting the sampler some time before samples are taken or allows discontinuous collection of samples. The stop relay causes a cessation of both timing and sampling when the appropriate step is reached. This allows the operator to predetermine the end of his sampling cycle and makes prompt attention to the unit unnecessary. In practice, a wide variety of sampling and non-sampling periods can be programmed.

Application

For certain routine sampling jobs, many of the features of this sampler would be unnecessary, but for other, more specialized work, they are invaluable. For instance, at the Brook-

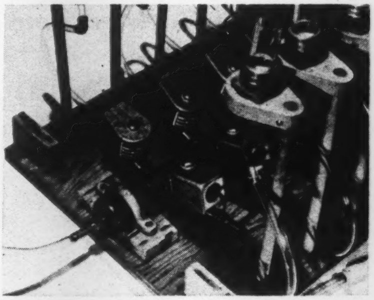

Fig. 2. Photograph of the sampling unit showing details of construction.

haven National Laboratory, a project was set up, in co-operation with the New York State Botanist, to determine the relationship of ragweed pollen concentration in the air to various weather conditions. In addition to routine longer period samples, hourly samples were wanted both before and after a cold frontal passage. The front was expected at 2400, outside normal working hours. Therefore, the machine was set up with a 1 hr. basic time cycle, turned on at 1700, delayed to 2100, sampled from 2100 to 0400 and shut off at 0400.

For another example from air pollution work, it might be desirable to take smoke samples before and after the onset and breakup of the nocturnal temperature inversion but all night samples might not be necessary. Let us say that inversion formation is expected at 1800 and the breakup at 0600. The sampler could be set out and turned on at 1600, take hourly samples to 2000, delay to 0400, sample to 0800 and shut off.

Discussion

Except for the brass tube which serves as the common outlet for the valves and could be replaced by an airtight container of any shape, all components are stock parts. The total cost of the components used is about $135.00. No machining is required and only simple hand tools and soldering equipment are necessary in assembly and wiring. The number of valves to be used and the type of stepping switch can be selected on the basis of individual requirements. In order to preserve versatility, however, the number of steps should be at least double the number of valves. A number of refinements and improvements are possible but this first model has proved so useful that an early description was thought desirable. Copies of the wiring diagram and specifications for components used are available upon request.

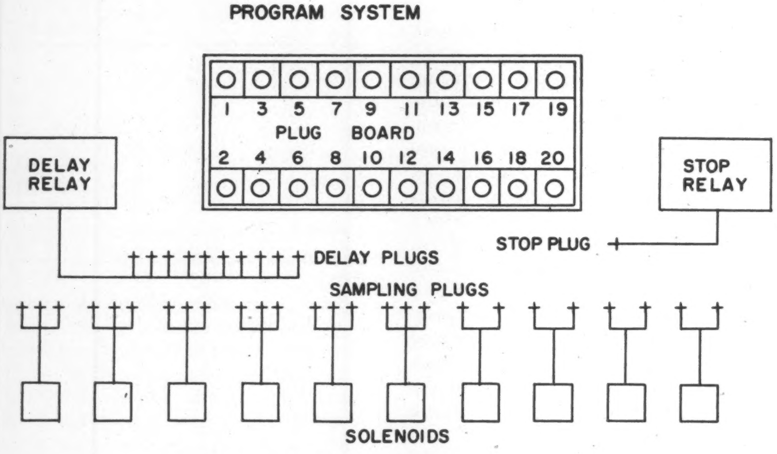

Fig. 3. Block diagram of the program system.

There is, of course, no reason why the timing and programming system could not be adapted to another purpose. Likewise, the sampling unit could be used with a far simpler timing circuit. The two together, however, make up an efficient and versatile unit which should meet the needs of many persons engaged in air sampling.

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Fifty-Years of Air Pollution Law*

HAROLD W. KENNEDY

Legal Counsel for the Air Pollution Control District
Los Angeles County, California

To most of us, 50 years seems a very long time. The past half century has seen revolutionary developments and magnificent advancements in most material spheres of man's endeavors. The legal mind, however, customarily thinks of 50 years of legal development as a ripple in the tide of the law. Many lawyers refer to cases decided in the year 1890, for example, as *recently* decided.

The reason for this attitude is the basic structure of the common law. Based as it is on revered and ancient precedent, the common law is characterized by a strong adherence to principal. Another characteristic of the common law is adaptability to new situations, but the process is usually a deliberate change rather than a sudden shift.

An intelligent review of the development of air pollution control law during the last half century may not be made without first recognizing the importance of the pre-1907 period. For with the exception of the one case of *Northwestern Laundry* v. *Des Moines,* 239 U. S. 486, 36 S. Ct. 206, 60 L.Ed. 396, (1916), the legal history of the pre-1907 period recorded leading United States cases which communicated the major principles of air pollution control law. The courts, during this early period, came to grips with the basic issues involved and laid a strong foundation upon which states and municipalities could rely in their efforts to abate air pollution problems in their local areas. The initial portion of this report will sketch the law as it appeared in 1907, as a backdrop to the developments of the last 50 years.

Common Law Nuisance

It should be noted at the outset that most of our early law and that of the English cases, dealt with air contamination as a part of the field of tort law commonly referred to as Nuisance. Smoke was considered to be a nuisance at common law, but it was not a nuisance *per se*. That is, in each individual case it had to be proved that the smoke was in fact injurious or offensive to the senses. In the case of a public nuisance it had to be proved that a large number of persons were affected. Blackstone reports a case in which the fumes from a lead smelter killed a neighboring farmer's corn and were held to be a nuisance (cited in appeal of *Pennsylvania Coal Company,* 96 Pa. 116. Earlier cases are collected in 77 English Reprint 816).

It is the prevailing and sound judicial view that the emission of dense smoke in populous communities is a public nuisance. In the case of *Glucose Refining Company* v. *City of Chicago,* 138 Fed. 209, 215 (1905), the court said:

"The bill admits the issuance of dense smoke, and it is a matter of common knowledge, of which the court may take cognizance (*State* v. *Tower*) (Mo. Supp.) 84 S.W. 12; *Moses* v. *United States,* 16 App. D.C. 428; *Field v. Chicago, supra*), that smoke emitted from a tall chimney is carried over a wide territory, and that when dense, it deposits soot to such an extent as to injure property and health wherever it spreads."

A good statement on the general and prevailing rule in regard to smoke as a public nuisance, was made by the Supreme Court of Indiana in the case of *Bowers* v. *City of Indianapolis,* 162 Ind. 105, 81 N.E. 1097 at 1098, 13 Ann. Cas. 1198, (1907). The court upheld an ordinance of the city of Indianapolis providing:

"The emission of dense, black . . . smoke from any smokestack used in connection with any stationary . . . furnace of any description within . . . the city . . . except as a private residence, shall be deemed and is hereby declared to be a public nuisance."

The court said:

"The question we have to deal with is not as to the authority to regulate the emission of dense smoke in a sparsely inhabited locality, wherein the act could only result in the creation of a private nuisance, but of the right to prevent the emission of dense black or gray smoke (for so we construe the ordinance) within the corporate limits of a populous city, wherein, if there be no regulations upon the subject, the smoke from scores of steam plants must, in the nature of things, often cover the city as with a pall, thereby impairing the health and comfort of thousands, and casting grime upon every exposed object. If there is anything in the principle of the greatest good to the greatest number, or in the declared authority of government reasonably to regulate the use of property for the common good, it must be affrmed that power exists to deal with a condition which renders life in a great manufacturing city little short of impossible."

As stated by Lord Romilly in *Crump* v. *Lambert,* L.R. 3, Eq. 409, 15 Week. Rep. 417 (England), (1867),

"The real question in all cases is the question of fact, namely, whether the annoyance is such as to materially interfere with the ordinary comforts of human existence."

Need For Legislation: Nuisance Per Se

Long before Blackstone's time it was recognized that the law of nuisance was not adequate to take care of the situation in an urban community where there were a number of sources of air pollution. In England, the first smoke abatement law appears to have been enacted in the reign of Edward I, in the year 1273. In 1307 one offender of this law, which prohibited the use of the coal, as detrimental to health, was condemned and executed. In 1661 John

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* Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

Evelyn wrote a book on the smoke nuisance in London (*Fumifugium: or, The Inconvenience of the Aer,* and *Smoake of London Dissipated, Together With Some Remedies . . .,* reprinted by the National Smoke Abatement Society, London 1933). His remedy was quite simple. All industry was to be moved to the leeward side of the city and sweet smelling trees planted in the city.

The need for enlargement of the public nuisance category was seen by the court in the Missouri case of *State* v. *Tower,* 185 Mo. 79, 68 L.R.A. 402, 84 S.W. 10 (1904).

The court said:

"In a word, we assume that the basis of this contention is that, because at common law thick, dense smoke was not deemed a nuisance *per se,* but depended on the character of the smoke, the quantity, the location, and the circumstances, therefore it was not competent for our General Assembly to declare the emission or discharge into the open air of dense smoke within a city of 100,000 inhabitants a nuisance. The power of the General Assembly to pass all needful laws, except when restricted by the state or federal constitution, is plenary, and the Legislature has the power to declare places or practices to the detriment of public interest, or to the injury of the health, morals, or welfare of the community, public nuisances, although not such at common law. The General Assembly, in the exercise of the police power, may declare that a nuisance which before was not a nuisance . . . Even at common law smoke alone in certain circumstances constituted a nuisance; that is to say, when it produced a tangible injury to property as by the discoloration of buildings, injury to vegetation, the discoloration of furniture, and like cases.

"It was entirely competent for the Legislature to take cognizance of the fact, known to all men, that the emission and discharge of dense smoke into the atmosphere of a large and populous city is of itself a nuisance . . . and one calculated to interfere with the health and comfort of the inhabitants thereof, and to declare it a nuisance *per se* . . . We have no hesitancy in holding that it was entirely competent for the Legislature to declare the emission of dense smoke in the open air in a city of 100,000 inhabitants a nuisance *per se.*"

The rule of the *Tower* case that the state, under its police power could declare smoke a nuisance *per se,* even though not a nuisance *per se* or a nuisance at common law, found strong support in cases decided at the beginning of the post 1907 period. *Northwestern* v. *Des Moines, supra, State* v. *Chicago, M & St. P. Ry. Co.,* 114 Minn. 122, 130 N.W. 545, 546, Ann. Cas. 1712 B, 1030 (1911).

The validity of regulating statutes or ordinances does not depend upon whether or not the act prohibited is a nuisance but depends instead upon whether or not the law comes within the constitutional limitations and, in the case of a city or county, whether or not it has power under its charter or constitutional statutory provisions to pass such a law.

It is either within the police power of a municipal corporation or under specific power under charter or statute to adopt reasonable regulations to protect the public, health, safety and welfare. Without a doubt it is within the competence of a state legislature to confer upon municipalities power to enact ordinances to protect against atmospheric contamination or pollution, such as smoke ordinances, as constituting a proper exercise of municipal police power or power to safeguard against nuisances.

7 McQuillin on Municipal Corporations, 3rd Ed. p. 469, 470.

Probably the earliest United States case upholding a municipal smoke control ordinance is that of *City of New Orleans* v. *Lambert,* 14 La. Ann. 247 (1859), where the Louisiana Supreme Court reinstated an injunction by a city against the operation of a blacksmith shop because it exuded offensive odors, smoke, and was a nuisance, all in violation of a city ordinance. The court gave note to the fact that the police power covers such cases.

Validity As To Due Process

Subsequent to 1894, based upon the decision handed down in *Lawton* v. *Steele,* 152 U. S. 133, 14 Sup. Ct. 499, 38 L.Ed. 385, it became well settled that any provision of a statute or ordinance regulating a nuisance, such as the smoke nuisance, is valid in so far as the due process clause is concerned, if it is reasonably necessary for the accomplishment of the purpose and for the public welfare generally, and if it is not unduly oppressive, nor arbitrarily interferes with private business or imposes unusual or unnecessary restrictions upon a lawful occupation. As was said by Mr. Justice Brown, in *Lawton* v. *Steele, supra,*

"While the legislature has no right arbitrarily to declare that to be a nuisance which is clearly not so, a good deal must be left to its discretion in that regard, and if the object to be accomplished is conducive to the public interests it may exercise a large liberty of choice in the means employed."

It would seem that no certain and satisfactory limitation upon the legislative discretion, in the exercise of the police power, can safely be declared in advance for application to very many cases that may subsequently arise (*Moses* v. *United States, supra*).

Availability of Control Equipment

One of the major court decisions rendered prior to 1907 having significance to the use of scientific appliances or controls was the case of *People* v. *Detroit White Lead Works,* 82 Mich. 471, 46 N.W. 735 (1890). As a result of the decision of this case the rule became well established for a number of years thereafter that whenever a business becomes a nuisance, it must give way to the rights of the public and the owners thereof must either devise some means to avoid the nuisance or must remove or cease the business, even though the business is carried on in a careful manner and nothing is done which is not a reasonable and necessary incident to the business and even though there may be no smoke consuming appliance that will under all circumstances prevent the nuisance. It is to be noted, however, that later cases, and especially those of recent vintage show a tendency away from the ruling of the *Detroit White Lead case.* A treatment of these more recent decisions will be made later in this discussion.

Summary: Pre-1907 Period

It may be said, in summarizing the accomplishments of the pre-1907 period, that the following aspects of air pollution control law represent the majority, if not all, of the basic principles which became settled and accepted.

(1) Although at common law smoke and other air contaminants were not considered to be a nuisance *per se* the legislature can declare air contaminants to be a public nuisance and the courts will not invalidate

such legislative acts, provided that the legislative declaration is reasonably clear and certain.

(2) A statute or ordinance will be valid as far as due process is concerned, if it is reasonably necessary for the benefit of the public welfare, and if it is not arbitrary or oppressive.

(3) The state has the power to confer upon municipalities the power to enact ordinances for the purpose of regulating air pollution as constituting a proper exercise of the police power of the municipality.

(4) The courts take judicial notice that dense smoke is a nuisance or at least harmful enough to be declared a nuisance.

The Last Fifty Years

Whereas it might be interesting to trace the progress of the law since 1907 in chronological order of the decided cases, such an approach would prevent proper analysis of the issues decided. Consequently, for convenience we shall take up each issue separately and discuss the cases bearing upon it.

Although the cases decided prior to 1907 rather clearly established that the state could, under its police power, prohibit or regulate the emission of smoke or fumes it was not until 1916 that the substantive law of air pollution control was enriched with the clear and concise opinion rendered in *Northwestern Laundry* v. *Des Moines, supra.* This case, as do a number of cases in the state courts, holds that the ordinances merely prohibiting the emission of dense smoke in cities or populous neighborhoods, and also ordinances that prescribe a definite scientific standard for the density of smoke, such as the Ringelmann Scale, are valid so far as constitutional limitations are concerned. The smoke may be forbidden without reference to the time or quantity or emission or the immediate surroundings.

In the *Des Moines* case, the laundry filed a bill in equity in the United States District Court in Iowa against the City of Des Moines, and the smoke inspector and members of the smoke abatement commission of that city, to enjoin the enforcement of a Des Moines ordinance providing that the emission of dense smoke in portions of the city was a public nuisance. It was claimed that the ordinance was void under the due process and equal protection clause of the Fourteenth Amendment in that, among other things, the ordinance in providing for the use of Ringelmann Smoke Chart, prescribed arbitrary tests of degrees of density. The standard of efficiency required the remodeling of practically all furnaces. It forbade remodeling or new construction without a license and gave discretion to the smoke inspector and abatement commissioners to prescribe requirements. The court held the ordinance valid and dismissed the bill upon its merits, saying:

"So far as the federal constitution is concerned we have no doubt the state may by itself, or through authorized municipalities, declare the emission of dense smoke in cities or populous neighborhoods a nuisance and subject to restraint as such; and that the harshness of such legislation, or its effect upon business interests, short of a merely arbitrary enactment, are not valid constitutional objections. Nor is there any valid federal constitutional objection in the fact that the regulation may require the discontinuance of the use of property, or subject the occupant to large expense in complying with the terms of the law or ordinance. Recent cases in this court are *Reinman* v. *Little Rock*, 237 U. S. 171, 59 L. Ed. 900, 35 S. Ct. Rep. 511; *Chicago and A. R. Co.* v. *Tranberger*, 238 U. S. 67, 59 L. Ed. 1204, 35 Sup. Ct. Rep. 678; *Hadacheck* v. *Sebastian*, decided December 20, 1915, (239 U.S. 394, Ante, 348, 36 Sup. Ct. Rep. 143)."

"That such emission of smoke is within the regulatory power of the state has been affirmed by state courts. *Harmon* v. *Chicago*, 110 Ill. 400, 51 Am. Rep. 698."

To the same effect see also the following authorities:

7 McQuillin: Municipal Corporations, 3rd Ed, page 475, Section 24.495;

37 Am. Jur. 939, Note 9, Section 295;

43 Corpus Juris 431, Section 571.

39 Am. Juris 336-338, Section 54;

1918 B Ann. Cas. 173;

6 A.L.R. 1575;

58 A.L.R. 1225; 18 Cal. Jur.-838, Section 141;

46 Cent. Law Jour., 151;

Manual of Ordinances and Requirements, published by Smoke Prevention Assoc. of America, Inc.; p. 24 (1940).

The passage of time has taken nothing away from the authority of cases like *Northwestern Laundry* v. *Des Moines, supra.* It upheld the right of a city, after receiving statutory authority, to forbid the emission of dense smoke in cities or populous neighborhoods. Recent cases consider the problem settled. In *Board of Health of Weehawken Township, Hudson County* v. *New York Central Railroad* (1950) 4 N. J. 293, 72 A. 2d 511 at 514, the court said:

". . . There are no constitutional restraints upon state actions against the emission of dense smoke injurious to the common welfare; the only requirement is that the regulation be free from arbitrariness. *Northwestern Laundry Co.* v. *Des Moines, supra.*"

Refinements of Air Pollution Control Law

With the inclusion of the decision of the *Des Moines* case in the body of air pollution control law, legislatures, municipalities and local control districts saw a fulfillment and completion of the essential and legal grounds necessary to provide them with sufficient power and confidence to forcefully attack their immediate air pollution problems.

For the most part the significant cases in the field of air pollution control, in addition to those already discussed, have greatly aided the administration and application of existing statutes and ordinances by defining with various refinements the nature of such laws. These refinements as presented by specific problems are the subject of the following portion of this discussion.

Liberal Construction of Regulations

The liberal attitude of some courts toward air pollution control regulations is illustrated by the following quotation from *Penn-Dixie Cement Corp. v. City of Kingsport,* (1949) 189 Tenn. 450, 225 S.W. 2d 270, 275:

"Ordinances to preserve the public health have been liberally construed and the authorities have gone to great length in enumerating the implied powers of municipalities to enact laws to protect the community from infectious and contagious diseases, from bad water, against nuisances injurious to health and noxious odors and gases. Inasmuch as the provision of the public health and the safety of the inhabitants is one of the chief purposes of local government, all reasonable ordinances in this direction have been sustained."

The court in *People* v. *Consolidated Company of New York, Inc.,* 116

N.Y.S. 2d 555 (1952), found that the Smoke Control Bureau of the City of New York acted under the police power of the City of New York in promulgating its rules and regulations, and that such rules and regulations are remedial and must be liberally construed.

For other cases where the court used a liberal construction, see *Department of Health of City of N. Y.* v. *Philip and William Ebling Brewing Co.*, 38 Misc. 537, 78 N.Y.S. 13 (1902), and *People* v. *Long Is. R. Co.*, 31 N.Y.S. 2d 537 (1942).

Requisite of Reasonableness

Any ordinance or statute under the police power must be reasonable, and for that reason must regulate or forbid something which is or could be considered detrimental to the public peace, health, safety, morals or general welfare. If any set of facts may be supposed as to which a law or ordinance is reasonable, or if reasonable minds may differ on the question, the enactment will be sustained. *Matter of Miller* (1912) 162 Cal. 687; *Clemons* v. *City of Los Angeles* (1950) 36 Cal. 2d 95, 98-99, 222 P. 2d 439; *Miller* v. *Board of Public Works*, 195 Cal. 477, 488-490, 234 P. 2d 38. Where the ordinance or statute passes this test, a naked violation of the ordinance is all that need be shown.

The legislature has a wide discretion in determining what is a nuisance and what is not, and what may be regulated under the police power. In doubtful cases, the determination of the question by the legislative body is conclusive. The courts will not interfere unless the law results in needless oppression, and will not question the wisdom of the legislation. But the courts are not limited to the face of the law itself. The courts may look behind the law and determine from competent extrinsic evidence whether or not the law is reasonable. *Moses* v. *United States, supra; Bradley* v. *District of Columbia*, 20 App. D.C. 169; *State* v. *Tower, supra. Cincinnati* v. *Burkhardt*, 30 Ohio Cir. Ct. Rep. 350, Ann. Cas., 1918 B. 174, (1908).

In the case of *Moses* v. *United States, supra,* the court said:

"The policy of adopting a regulation to meet the conditions is a matter purely and exclusively within the province of the legislative department. The judiciary can only interfere with the exercise of the power where it is manifest that the regulation has no real or substantial relation to objects within the police power, and constitutes a palpable invasion of private rights."

It can be seen that what is *reasonable* depends upon the circumstances. No hard and fast rule can be established for all cases. It has been urged that legislation regulating the use of bituminous coal is unreasonable, especially in a district where soft coal is produced in large quantities, and where such coal is universally used for fuel. It is argued that to enforce a law of this character would require industry to use expensive anthracite or other smokeless fuel causing great hardship, and perhaps, driving many plants from the city. This contention was easily refuted by the Supreme Court of Illinois in the case of *Harmon* v. *Chicago,* 110 Ill. 400, which disposed of the objection as follows:

"It may be that some, and, perhaps, very great inconvenience would be experienced by a rigid enforcement of the provisions of this ordinance. How that may be this court cannot know. What powers the city council may exercise under the general law or under its police powers is a question of law to be determined by the courts; but when the city council will exercise the powers with which it is clothed rests in its legislative discretion, and the consequences that may flow from the enforcement of ordinances enacted within the powers conferred, rests alone upon the body enacting them, and with which the courts have no concern."

In *State* v. *Pond,* 93 Mo. 618, the court said:

"With the policy of the law, the wisdom or want of it in its enactment, we have no concern; that belongs to the domain of the legislature. Our business is to declare what is law and not to make law."

Actual damage in a particular case need not be shown to sustain a conviction under an ordinance. In *State* v. *Mundet Cork Co.,* (1952) 8 N. J. 359, 86 Atl. 2d 1 at 6, the court said:

"Further, *actual* injury to health or property is not necessary to the proof of conviction of violation of the ordinance, since whether persons or property are or may be injured by the continued exercise of the prohibited conduct or industrial operation is relative to the question of reasonableness of the ordinance and not to the question of fact as to what constitutes violation thereof."

After holding a smoke ordinance prohibiting the emission of smoke of greater density than No. 2 Ringelmann to be a valid public health measure, the court in *Board of Health of Weehawken Township* v. *New York Central Railroad* (1950) 4 N. J. 293, 72 Atl. 2d 511, 514-515, said:

"At common law, an action of nuisance will lie for substantial discomfort or inconvenience. But the inconvenience must be more than fanciful; it is not actionable unless it is one 'materially interfering with the ordinary comfort physically of human existence, not merely according to elegant or dainty modes and habits of living, but according to plain and sober and simple notions among the English People.' *Walter* v. *Selfe* (1851) 4 DeG. & Sm. 322. The common law judges by no Spartan standards. The loss of even one night's sleep is not deemed a trivial matter. *Andreae* v. *Selfridge* (1937) 3 A.E.R. 261; Salmond on the Law of Torts (10th Ed. 1945) 224. Of course, the standard of convenience and comfort varies according to local conditions and needs. It suffices to say as to this that the conditions constituting a nuisance at a given time and place may not be a nuisance at another time and place. And it may be added that the complexities of our modern society due in large part to congestion of population and concentration of industry and business impose an ever increasing demand for individual concessions to the common good . . ."

Illustrative Cases Holding Regulations Valid: Reasonable; Reasonable Classifications; Certain

In the case of *City of Brooklyn* v. *Nassau Electric R. Co.*, 61 N. Y. S. 33, (1899), an action was brought to recover from defendant a penalty of $100.00 for using soft coal in contravention of a statute providing:

"No factory, engine room or electrical station shall use what is known as soft coal for fuel . . . within a radius of four miles of the city hall . . ."

The court held that it was within the police power of the legislature to declare that the burning of soft coal within certain prescribed limits of the city was detrimental to the public welfare and that the same should be forbidden as a benefit to the general public.

"Ordinances must not only be reasonable and within the power of the municipality to enact them under its charter, but must affect each member of the community alike. They should neither favor nor discriminate against any person or class of persons or any particular portion of the municipal territory. Their burdens and their benefits should rest equally upon all." (*People* v. *Lewis*, 86 Mich. 273, 49 N.W. 140, (1891))

In the above case the court held as not unreasonable an ordinance which provided that private residences and steam boats be excluded from the ordinance declaring the emission of dense smoke that caused the deposit of soot on any surface within the corporate limits to be a public nuisance.

In the case of *State* v. *Tower, supra,* the general assembly of the state had passed an act in 1901 which made the *emission or discharge into the open air of dense smoke within the corporate limits of this state which now have or may hereafter have a population of 100,000 inhabitants* a public nuisance. The statute exempted owners of premises who may be able to show to the satisfaction of the court that there is no known practical device to prevent the emission of dense smoke. The court upheld the Missouri statute as valid and reasonable.

In the case of *Moses* v. *United States, supra,* sustained by the court in the case of *Bradley* v. *District of Columbia, supra,* an act of Congress provided:

"The emission of dense or thick black or gray smoke or cinders from any smoke stack or chimney used in connection with any stationary engine, steam boiler, or furnace of any description within the District of Columbia shall be deemed and is hereby declared to be a public nuisance; provided that nothing in this act shall be construed as applying to chimneys of buildings used exclusively for private residences."

The act provided for a fine of from $10 to $100 for each offense and that every day in which the provisions were violated, constituted a separate offense.

The judgment of conviction by the police court of the District was affirmed and the ordinance upheld. The court held that the power of Congress to enact regulations affecting the public health and comfort was the same as that of the legislatures of the several states within their respective territorial limits.

In sustaining the ordinance the court quoted with approval from *Lawton* v. *Steele, supra,* as follows:

"'To justify the state in thus interposing its authority in behalf of the public it must appear, first, that the interests of the public generally, as distinguished from those of a particular class, require such interference; and, second, that the means are reasonably necessary for the accomplishment of the purpose, and not unduly oppressive upon individuals. The legislature may not, under the guise of protecting the public interests, arbitrarily interfere with private business, or impose unusual or unnecessary restrictions upon lawful occupations. In other words, its determination as to what is a proper exercise of its police powers is not final or conclusive, but is subject to the supervision of the courts.'"

The court further stated:

"Nothing short of satisfactory proof that under no circumstances could the emission of the forbidden smoke occasion material injury, inconvenience, or discomfort to the public would, at most, be sufficient to show that the statute, under the guise merely of the public interest, was an unwarranted invasion of private right."

In *Cincinnati* v. *Burkhardt*, 30 Ohio Cir. Ct. Rep. 350, Ann. Cas., 1918 B, 174 (1908) an ordinance which provided for the measurement of the density of smoke by use of a color scale was upheld.

In *Bower* v. *City of Indianapolis,* 162 Ind. 105, 81 N.E. 1097, 13 Ann. Cas. 1198 (1907), an ordinance was upheld which declared the emission of dense smoke within the city, except from private residences, to be a public nuisance. The state had given cities authority by statute to declare what should constitute a nuisance.

In re Junqua, 10 Cal. App. 602, 103 Pac. 159, (1909), was a case in which an ordinance of the city of Sacramento prohibiting the escape of any soot from smoke stacks or chimneys of any furnaces using distillate or crude oil was upheld.

In *City of Rochester* v. *Macaulay-Fien Mill Company,* 199 N. Y. 207, 92 N.E. 641, 32 L.R.A. (N.S.). 554, (1910), the court held reasonable an ordinance of the City of Rochester which provided for the adoption of the standard of the Ringelmann Scale, prohibited dense smoke during the day except from between 5 a.m. and 7:30 a.m., and which permitted the emission of dense smoke for 5 min. in every 4 consecutive hrs.

In *People* v. *Tatje,* 121 N. Y. Supp. 2d 147, (1953) the defendant was charged with unlawfully causing, suffering and allowing dense smoke to be emitted into the open air from a chimney attached to a boiler in the premises under his control. The court held that the rule prohibiting emission of dense smoke from fuel burning equipment was not invalid as conflicting with penal law and Health Board Regulations requiring landlords to furnish heat and hot water to tenants.

The case of *Ballentine* v. *Nester,* 350 Mo. 58, 164 S.W. 2d 378, (1942), is one of the leading cases on the subject of reasonableness of air pollution control ordinances. In the *Ballentine* case the Supreme Court of Missouri, held valid an ordinance of St. Louis, passed in 1940, regulating the smoke nuisance.

The petitioner in the case had been convicted of violating a section of the St. Louis Ordinance prohibiting the use of coal, having a volatile content of more than 25% on a dry basis. In his petition for a writ of habeas corpus, the petitioner asserted that the ordinance violated the Fourteenth Amendment of the Federal Constitution, the Revised Statutes of Missouri, and the St. Louis Charter. The Court denied the petition, upholding the conviction and the validity of the ordinance.

In reaching its decision, the court cited and quoted with approval from the case of *Northwestern Laundry* v. *Des Moines, supra,* and stated:

". . . Nor do we think this section, in regulating the use of coal, violates the due process and the equal protection of the Fourteenth Amendment of the Federal Constitution."

As to the claim of petitioner that the ordinance did not always regulate noxious gases, the Court said:

"It is true the ordinance makes only the emissions of dense smoke unlawful; it contains no provision that tends to regulate or prevent the discharge of deleterious gases into the air. The legislative authorities may classify with reference to an evil to be prevented, and legislation designed to prevent one evil is not void because it does not prevent another."

The case of *Glucose Refining Company* v. *City of Chicago,* 138 Fed. 209 (1905), involved a Chicago ordinance passed in 1903, which ordinance declared that the emission of dense smoke was a public nuisance, and prohibited the emission of dense smoke for more than 3 min., or, in case fire boxes are being cleaned or new fires started, for more than 6 min. in any hour of day or night.

The complainant attempted to enjoin enforcement of the ordinance, asserting that it violated the Federal Constitution. The court denied the injunction on the ground that the bill admitted the issuance of dense smoke, and the court took judicial notice of the fact that such smoke was a nuisance and spread over a large territory.

In 1955 the United States Supreme Court (351 U. S. 990, 100 L.Ed. 1503) dismissed an appeal from the decision handed down by the Appellate Department, Superior Court, Los Angeles, involving four separate cases each of which involved one or more charges and convictions of *smog* violation. *People* v. *Plywood Manufacturers of Calif.; People* v. *Shell Oil Co.; People* v. *Union Oil Co.; People* v. *Southern Calif. Edison Co.;* 137 C.A. 2d Supp. 859; 291 P. 2d 587.

The defendants stood charged and convicted of violating Section 24242 of the Health and Safety Code. Section 24242 provides:

"A person shall not discharge into the atmosphere from any single source of emission whatsoever any air contaminant for a period or periods aggregating more than three minutes in any one hour which is:

"(a) As dark or darker in shade as that designated as No. 2 on the Ringelmann Chart, as published by the United States Bureau of Mines, or

"(b) Of such opacity as to obscure an observer's view to a degree equal to or greater than does smoke described in subsection (a) of this section." Directly involved was subdivision (b) relative to opacity of emission. The Appellate Department, after recalling its prior decision in *People* v. *International Steel Corp.* (1951), 102 Cal. App. 2d Supp. 935, 226 P. 2d 587 that the standard made use of in subsection (a) is sufficiently definite to satisfy due process, went on to say:

"Subdivision (a) only begins to solve the problem of the discharge of contaminants into the air; it does not touch smoke and other substances too light in shade to come up to Ringelmann No. 2. They may be so substantial in nature, however, that they make it impossible to see an object on the other side. We have all seen very white smoke that shut out the view completely. Again they may obscure the view to a lesser degree than totality . . .

"We may, therefore, express the test of subdivision (b) in simple terms; it condemns smoke or any other contaminant that is at least as hard to see through as is smoke which is as dark or darker than Ringelmann No. 2. There is nothing mystic or incomprehensible about such a statement."

The court in upholding the validity of subsection (b) of the statute dismissed the contention made by appellants that Section 24242 was unconstitutional for uncertainty under the theory that an ordinary person having no special training, will not be able to tell whether certain smoke is as dark as Ringelmann No. 2, or whether its opacity equals that of smoke matching Ringelmann No. 2, by stating:

"A statute is invalid if its terms leave that which it attempts to control shrouded in uncertainty, but a statute which declares an act, identified with certainty; to be unlawful is not rendered unconstitutional because the act, as a fact, may not be readily identifiable by the common man as that forbidden by the statute."

Illustrative Cases of Reasonable Classifications

In *Moses* v. *United States, supra,* the statute exempted chimneys of buildings used exclusively for private residences, while declaring the emission of dense or thick black or gray smoke of cinders from smoke stacks or chimneys to be a public nuisance. The statute was upheld.

In *State* v. *Tower,* 134 Mo. App., 352, 114 S.W., 1104, (1908) the court sustained a conviction under a Missouri statute prohibiting dense smoke in cities of more than 100,000 except where no device for compliance existed. It was shown that the defendant was using a boiler to which no device could be attached.

In *Atlantic City* v. *France,* 75 N.J.L. 910, 70 Atl. 163, 18 L.R.A. (N.S.) 156 (1908), the court upheld an ordinance which made it unlawful to permit the emission of dense smoke from any stack connected with any engine or locomotive within the city limits, which smoke contained soot or other substances in sufficient quantity to cause injury to the health or damage to property within the corporate limits of the city, and which made no distinction between locomotive engines operated on railroads and any other kind of engine.

Legality of Automotive Exhaust Control Devices

Scientific studies and tests have left little doubt that automotive exhausts emit irritating substance in the nature of incombustible gasoline. The formation and enforcement of effective measures to control this source of pollution continues to be a serious problem with air pollution control officials.

The courts have upheld the right of the legislative branch of government to prescribe the methods, regulations, and restrictions to be imposed as a means of achieving the desired elimination of air pollutants as a proper exercise of the police power as long as the legislative determination is not arbitrary and unreasonable (*Ballentine* v. *Nester* 350 Mo. 58; 164 S.W. 2d 378; *Northwestern Laundry Company* v. *Des Moines,* 239 U. S. 486; 60 L.Ed. 396; 36 S. Ct. 206).

The County Counsel of the County of Los Angeles examined into the legality of requiring a control device on every new motor vehicle, and on October 27, 1953, an opinion was released holding that the Board of Supervisors sitting as the Air Pollution Control Board, after notice and hearing competent testimony that automobile exhaust gases are a material contribution to the smog problem, could require every new automobile sold for use in Los Angeles County, including those sold in cities, to be equipped with a device which would eliminate or reduce exhaust gases, or set a time limit after which any new automobile, bus or truck would be equipped with a device approved by the Air Pollution Control District. The County Counsel's opinion stated in part as follows:

"Our answer is that the rule-making power of the Board of Supervisors, sitting as the Air Pollution Control Board, is broad enough to cover almost any conceivable situation in connection with the control of air pollution in this County. Such powers, however, may not be exercised arbitrarily, capriciously, or unreasonably. Board action must be based on proven facts or sound scientific opinion. As the engineers and chemists discover new sources of, or new remedies for air pollution, the Board's power extends to these new sources and remedies. Answering your question more specifically, the Board will have the power to require motor vehicles to be equipped with a device to eliminate the emission of air contaminants as soon as such a device is perfected, shown to be effective, available on the market and the requirement of its use is found to be reasonable . . .

"However, we are informed by the Air Pollution Control District engineers that there is no device on the market as yet which will reduce or eliminate the emission of fumes from motor vehicles. One device is being tested, another is still in the designing stage. It is not known whether either will work. Neither is it known how long it will be before some such device, after being proved practicable, will be available commercially.

Until such a device is perfected and on the market, any rule requiring the use of the device is arbitrary, capricious and void, unless the hazard to life and property is so great that a rule would be justified forbidding the sale or use of motor vehicles in this County. From the facts given to us, the Board could conclude that there is no such emergency now in Los Angeles County. Once a satisfactory device is perfected, shown to be effective for the purpose and practicable in operation, then the regulation proposed could be adopted, allowing sufficient time before it becomes effective to get the device on the market in reasonable quantities. As it is impossible to tell when such a device may be invented, or if invented, when perfected for motor vehicle use and shown to be practicable, no such regulation could be adopted now to be effective at a future date.

"We conclude that the rule you suggest, with certain modifications, can be adopted when the required device is available, but not until then."

Illustrative Cases Holding Regulations Invalid; Unreasonable; Uncertain; Insufficient Power in Local Body

In the case of *Department of Health of the City of New York* v. *Philip and William Ebling Brewing Company,* 38 Misc. 537, 78 N.Y.S. 13, (1902), the Court refused to convict the defendant for allowing gas to escape from its furnace where it was not shown that the gas was detrimental or annoying to any person, although the ordinance involved literally prohibited the emission of all smoke or gas from furnaces. The ordinance (Section 134 of the Sanitary Code of New York City) provided:

"Nor shall any . . . person . . . allow any smoke . . . gas, steam or offensive odors to escape . . . from any . . . building . . ., and every furnace employed . . . shall be so constructed as to consume or burn the smoke arising therefrom."

The court said:

". . . It appears that the defendant has adopted and uses a pattern of furnace designed to burn and consume smoke; that the matter carried off from the firebed does not pass directly into its chimney, but passes first through a process that burns and consumes all the solid matter in the escaping product of combustion, so that whatever passes into the chimney is in the form of a gas, without ash, soot, or dust.

". . . The defendant's proof establishes that whether the flue of its chimney carries off imperceptible gas or visible smoke, in neither case is any feature of nuisance to any resident of the city possible, nor has anyone living in any direction from its premises suffered any injury, annoyance, inconvenience, discomfort, or hurt. If the provision adopted by the Board of Health, however, is to be literally applied, these considerations are immaterial, because the section prohibits the escape of smoke under any circumstances.

". . . If it had not been proved before me in this case, I think that the Court would take judicial cognizance of the fact that no fire can be burned without giving off as a product of combustion an exhalation visible as smoke or invisible as gas. To prescribe that a furnace should be used without allowing any smoke or gas to be given off calls for as little possibility of compliance as to require that it be used without permitting combustion, and yet that is what this section of the Sanitary Code literally requires. It cannot be supposed that the legislature intended to require the impossible or to close every furnace in our city for the promotion of a better atmosphere. To give this section, therefore, a reasonable and working application, the attempt to construe it literally must be abandoned, and something further looked to than the phraseology in its unqualified significance.

". . . All the prohibitory provisions of that Code are designed to prevent actions that are calculated to work a detriment to some person. To accomplish that is the reason and excuse for interfering with the liberty of each individual to do as he pleases with his own. When, therefore, the legislature enacted as a part of the Sanitary Code that no gas or smoke should be allowed to escape from a furnace, I think it must be understood with the implied qualification, 'to the detriment or annoyance of any person.'"

See also: *People on complaint of Greene* v. *Long Island Railroad Company,* 31 N. Y. Supp. 2d 537, (1942).

In 1944 the Supreme Court of Illinois in the case of the *City of Kankakee* v. *New York Central Railroad Co.,* 387 Ill. 109, 55 N.E. 2d 87, held that the ordinance declaring the emission of dense smoke a nuisance which might be summarily abated by the building inspector, was unreasonable and arbitrary as applied to the defendant railroad in that it would prohibit the operations of such railroad. The ordinance did not define the terms and conditions which would guide the building inspector in the exercise of his discretion. The case is not too persuasive as a general proposition, however, and may be partially explained by poor draftsmanship.

In the more recent case of the *People* v. *San Pedro Lumber Company,* (Unreported, Appellate Department, Superior Court, Los Angeles County, California) CRA 2677, the Court agreed with the contention that a section of the Los Angeles Municipal Code was void for indefiniteness and uncertainty. The section in question read as follows:

"No person by himself, or his employee . . . shall cause, suffer or permit to be discharged from any source whatsoever within the city of Los Angeles, any unnecessary or unreasonable smoke, dust, soot, or fumes."

In so deciding, the Court stated:

"The effect of this provision is to prohibit the discharge of 'any unnecessary or unreasonable smoke,' without providing any standards of comparison for smoke or giving any clue to surrounding circumstances to be considered in determining whether smoke is unreasonable or unnecessary. The prohibition is in the alternative, so it definitively contemplates that smoke may be reasonable though unnecessary, or necessary though unreasonable, but it is not clear how either such conditions could be brought about. Neither does the ordinance state what may be recorded as a necessity, nor whether the necessity or reasonableness of smoke is to be determined from the standpoint of the person discharging it or otherwise. In short, the ordinance sets up no reasonably ascertainable standard by which a citizen can discover in advance whether his discharge of smoke will be held to violate the ordinance or not."

It is well to note at this point, that a number of cases that hold ordinances invalid have been decided on the ground that the local body did not have the power, under the particular state constitutional and statutory provisions or the charter of the local body, to declare dense smoke a nuisance. However, in such cases, the courts have usually admitted that the legislative body of the state had such power. It is in such cases, also, that the statement often appears that the municipality cannot make that a public nuisance which is not in fact such. Other decisions state that although the local body was given power to declare nuisances, it could not declare the emission of smoke a nuisance, because the mere emission of smoke was not in fact a nuisance or a nuisance *per se;* but that the state legislature could so declare.

For instance, in the case of *City of St. Louis* v. *Heitzeberg Packing and Provision Co.*, 141 Mo. 375, 42 S.W. 954 (1897) an ordinance of the City of St. Louis provided: *"The emission into the open air of dense smoke or thick gray smoke within the corporate limits of the City of St. Louis is hereby declared to be a nuisance."* The court held the ordinance void, stating that smoke alone was not a nuisance *per se*, and that the city could not declare that a nuisance which was not so in fact. The case was decided on the ground that the City of St. Louis did not have the power to declare smoke a nuisance, as its charter gave it the power only to declare nuisances on private and public property and the causes thereof, but did not specifically empower the city to declare the emission of thick smoke a nuisance.

In the case of *State* v. *Tower*, 185 Mo. 79, 84 S.W. 10, at page 12 (1904) the court stated that the question in the *St. Louis* case was not whether the *state* had the power, but whether the *city*, in the absence of a state law and in the absence of such power in its charter, could declare the emission of smoke a nuisance *per se*. This was also the basis of decisions holding ordinances of Cleveland and St. Paul unreasonable. *Cleveland* v. *Malm*, 7 Ohio Dec. 124, following *Sigler* v. *Cleveland*, 4 Ohio Dec. 166; *City of St. Paul* v. *Gilfillan*, 36 Minn. 298, 31 N.W. 49 (1886).

Statutes and Ordinances Not Based On Nuisance

The police power of the state, or of the municipality or other local agency when properly authorized by the state, extends to the regulation of air pollution, visible or invisible, without regard to whether the condition constitutes a common law or statutory nuisance.

In *Board of Health of Weehawken Township* v. *New York Central Railroad* (1952) 10 N. J. 294, 90 A. 2d 729, 735, the court said:

"The reason for a municipality making unlawful the emission of smoke is readily apparent. The issuance of dense smoke from a single chimney, in and of itself, may be altogether harmless and cause no inconvenience or damage to the public, but if smoke of like density issued from hundreds of chimneys, the contamination of the atmosphere would be substantial and the injury to the public considerable, yet for lack of the requisite elements of a public nuisance at common law, the municipality could obtain no relief by way of indictment. Ordinances making unlawful the emission of smoke are therefore obviously necessary and reasonable and a valid exercise of the local police power."

See also: *People* v. *International Steel Co.,* (1951) 102 Cal. App. 2d Supp. 935, 226 P. 2d 587.

In *State* v. *Mundet Cork Corp.*, (1952) 8 N. J. 359, 86 A. 2d 1, at 3-4, the court said:

"The emphasis in this type of ordinance for centuries has been placed on smoke regulation. (In response to a petition by the citizens of London, a royal proclamation was issued by Edward I in England in 1306 to prohibit artificers from using sea coal, as distinguished from charcoal. in their furnaces, and making use of sea coal a capital offense . . .) In more recent generations other air pollutants have been subjected to control . . . Ordinances designed to regulate and control air pollution in the interest of the public health and welfare have been held valid and enforceable in this State . . ."(1)

Validity Not Based on Nuisance

The validity of an ordinance or statute regulating the emission of smoke or fumes does not depend upon whether or not it is a nuisance. The validity depends entirely upon whether or not the law comes within the constitutional limitations and, in the case of a city, whether or not it has power under its charter or constitutional or statutory provisions to pass such a law. The police power permits the state to enact laws to forbid and regulate various practices to provide for the general welfare and comfort of the people, regardless of whether or not they constitute nuisances.

A leading case on the subject is the California case of *In re Junqua,* 10 Cal. App. 602, 605 (1909).

In this case the petitioner sought a discharge on a writ of habeas corpus to test the validity of a (Sacramento) city ordinance. The ordinance provided:

"It shall be unlawful for any person, firm or corporation to permit any soot to escape from the smokestack or from the chimney of any furnace within the City of Sacramento in which distillate or crude oil is consumed as fuel."

The petitioner claimed that the ordinance was unconstitutional and void on its face, as under the ordinance it made no difference how little soot was emitted. The court stated:

"That the police power is an inherent attribute of every state or commonwealth in the Union is a proposition which will readily be conceded. It is not only a power which inheres in the sovereignty of the states, but is a power the exercise of which by the states is indispensably essential to the health, peace, comfort and welfare generally of the inhabitants thereof . . .

"This power embraces the right to regulate any class of business, the operation of which, unless regulated, may, in the judgment of the appropriate local authority, interfere with the rights of others, for, as is said in *Dobbins* v. *City of Los Angeles*, 139 Cal. 179 (96 Am. St. Rep. 95, 72 Pac. 970), 'all property is subject to the police power.' In other words, the proposition cannot be maintained that the exercise of this power is confined to the regulation only of such interferences with the public welfare and comfort as some strictly within the common law definition of a 'nuisance.' (*Dobbins* v. *City of Los Angeles, supra.*)"

See also: *Buffalo* v. *George P. Ray Manufacturing Company*, 124 N. Y. 931, Ann. Cas. 1918 B, 174 (1910).

Not all courts have been so cooperative toward attempts to reduce air contamination.

For example, in the case of *Glucose Refining Company* v. *Chicago, supra,* the court said:

"... It is held in the case of *Harmon* v. *Chicago, supra,* that a Municipality cannot by ordinance make that a public nuisance which was not in fact such. The same rule is laid down in numerous cases and must be deemed a settled rule for the purpose of this motion."

In the case of the *State* v. *Chicago, supra,* the court stated:

"It is elementary that the legislature cannot prevent a lawful use of property by declaring a certain use to be a nuisance which is not in fact a nuisance, and prohibiting such use."

State Action to Abate Interstate Nuisance

In an equity action brought to enjoin a foreign corporation from discharging noxious gases from their works in Tennessee over large tracts of the state of Georgia, the United States Supreme Court in the case of *State of Georgia* v. *Tennessee Copper Company,* (1907) 27 S. Ct. 618, 51 L.Ed. 1038, upheld the injunction. Mr. Justice Holmes, writing for the Court said:

"This is a suit by a state in its capacity of quasi-sovereign. In that capacity the state has an interest independent of and behind the titles of its citizens, in all the earth and air within its domain. It has the last word as to whether its mountains shall be stripped of their forests and its inhabitants shall breathe pure air . . . If the state has a case at all it is somewhat more certainly entitled to specific relief than a private party might be."

Justice Harlan in a concurring opinion stated:

"Georgia is entitled to the relief sought, not because it is a state, but because it is a party which has established its right to such relief by proof."

Impairment to Health Not Necessary

Discomfort, inconvenience and annoyance to the public is sufficient, and impairment to health is not necessary, to render the emission of smoke and fumes a nuisance, and also to permit its abatement by statute. 39 Am. Jur. 337, Note 19, Section 54; *Moses* v. *United States,* 16 App. D. C. 428, 50 L.R.A. 532; *Judson* v. *Los Angeles Suburban Gas Co.,* 157 Cal. 168, 171, 173 (1910); *Dauberman* v. *Grant,* 198 Cal. 586, 48 A.L.R. 1244, 246 Pac. 319 (1926); *State ex rel Krittenbrink* v. *Whithnell,* 91 Nebr. 101, 135 N.W. 376, 40 L.R.A. (N.S.) 898 (1912).

In the case of *Moses* v. *United States, supra,* the court said:

"Without reference to statutory regulations or declarations in a particular case, any use of one's property, ordinarily lawful, may become a nuisance, not only when it produces injury to public health, safety and morals, but also when it occasions public inconvenience, or materially impairs the public comfort — 'the physical comfort of human existence.' "

In the California case of *Judson* v. *Los Angeles Suburban Gas Co., supra,* the plaintiff filed an action for damages and to abate a nuisance. The defendant had constructed gas works near plaintiff's home on the bank of the Arroyo Seco in Los Angeles. The smoke, odor and noise interfered with the comfortable enjoyment of plaintiff's property, but there was no evidence that plaintiff's health or that of his family was injuriously affected. The plaintiff complained that the smoke was so thick that it sometimes obstructed the landscape, had a penetrating odor, and at times strongly suggested a London fog.

The appellate court upheld the injunction and judgment for damages, and stated:

"In order that a judgment of this character may be upheld, it is not necessary that the health of plaintiff or of members of his household should have been impaired. It is sufficient if the odors, sounds, and smoke were offensive to the senses.

". . . A gas factory does not constitute a nuisance *per se.* The manufacture in or near a great city or gas for illumination and heating is not only legitimate but is very necessary to the comfort of the people. But in this, as in any other sort of lawful business the person conducting it is subject to the rule *sic utere tuo ut alienum non laedas,* even when operating under municipal permission or under public obligation to furnish a commodity . . . Nor will the adoption of the most approved appliances and methods of production justify the continuance of that which, in spite of them, remains a nuisance."

In the California case of *Dauberman* v. *Grant,* 198 Cal. 586, 48 A.L.R. 1244, 246 Pac. 319 (1926) the court held that the defendant could be enjoined from maintaining a nuisance where he maintained a smoke stack at such a low height that heavy black smoke and soot were carried into plaintiff's adjacent dwelling.

The court said:

"It was not necessary to the recovery of damages caused by the nuisance of smoke and soot to prove actual damage to plaintiff's property. She was entitled to recover for the personal discomfort and annoyance to which she had been subjected and it was a question for the trial court to determine the amount of compensation which she should receive."

See also: *State* v. *Mundet Cork Corp.,* (1952) 8 N. J. 359, 86 A. 2d 1.

Thus impairment to health need not be shown. However, in a proper case the court will take judicial notice of the fact that air pollution is injurious to health. *Penn-Dixie Cement Corp.* v. *City of Kingsport* (1949) 189 Tenn. 450, 225 S.W. 2d 270, 275. *Board of Health of Weehawken Township* v. *New York Central Railroad Co.,* (1950) 4 N. J. 293, 72 A. 2d 511, 514-515. In the *Penn-Dixie case,* the court said (at page 275):

"But this Court can and does take judicial cognizance of the fact that when the air is laden with a heavy cloud of smoke and dust that such a condition constitutes a nuisance and is detrimental to the health and safety of the public. When therefore the legislature confers upon a municipality authority to safeguard the public health, it is wholly unnecessary that the charter or general law should go further and declare that smoke and dust are detrimental to health. Everybody knows that it is . . ."

The *Weehawken Township* case (72 Atl. 2d at pp. 514-515) states:

"And there can be no doubt that the regulations under review have a substantial relation to the public health. Dense smoke, a carrier as it is of dust, soot and cinders, contaminates and pollutes the atmosphere and deteriorates its normal healthful attributes and qualities, and therefore cannot but be harmful to the public health, especially in populous areas. This is a matter of common experience, so much so that it is properly a subject of judicial notice."

Comparative Injury Doctrine, or Balancing the Equities

The doctrine of comparative injury, more commonly called *balancing the equities,* is accepted in some jurisdictions and denied in others, or accepted as to one set of facts and denied as to other situations. Based on equitable principles, it would seem to be properly applicable in cases of undue hardship. Yet the reasoning in the case of its denial is hard to answer; that in so far as plaintiff is denied a decree enjoining an actual nuisance, defendant in effect is giving an easement over plaintiff's land. This amounts to a taking of property for private use in violation of the Constitution. Where the defendant is required to pay plaintiff the reasonable value of his property, or the interest therein which is damaged, the effect is condemnation for the benefit of a private person who does not possess the power of eminent domain.

In *Anderson* v. *Souza,* (1952) 38 Cal. 2d 825, 243 P. 2d 497, the court said (at 38 Cal. 2d 842) that the owners of a private airport,

". . . must nevertheless conduct it with due regard for the rights of others, and if because of location the operation of such a business will result in depriving others of their property rights, it cannot be permitted, for to do so would, in practical effect, condemn the property of others in violation of constitutional guarantees. (*Hulbert* v. *California Portland Cement Co.,* 161 Cal. 239 (118 P. 928, 38 L.R.A.N.S. 436).)"

In *McIvor* v. *Mercer-Fraser Co.,* (1946) 76 Cal. App. 2d 247, at page 251, 172 P. 2d 758, the court analyzes the problem as follows:

"Appellants, without citation of authority, advance the novel proposition that the trial court erred in excluding evidence that after the excavation had been made and the respondents had protested, appellants offered to purchase respondent's property at its cost or the market price thereof, and thus 'make them whole.' Had the trial court permitted appellants to make such a showing it would have allowed them to take advantage of their own wrong, contrary to settled principles. (Civ. Code, sec. 3517). If appellants' theory were sound, one who coveted his neighbor's property could force a sale of the same by the simple expedient of injuring such property, of impairing the enjoyment thereof and cause the owner to sell or forego all right to damages by tendering to the owner the cost of said property to him or the market value thereof. This of course cannot be the law."

In *French Art Cleaners* v. *State Board of Dry Cleaners* (1948) 88 Cal. App. 2d 45, 46, 198 P. 2d 91, the question was raised on an application for a writ of supersedeas, and answered by the court as follows:

"The sole question then is whether the showing made by petitioner is such as will justify this court in exercising its inherent power in his behalf. We think that it is. This conclusion is not based upon a balancing of conveniences or hardships, which is not the proper test . . . but upon a consideration of the respective rights of the litigants, which contemplates the possibility of an affirmance of the decree as well as of a reversal."

The question was raised in a little different form in *Guttinger* v. *Calaveras Cement Co.* (1951) 105 Cal. App. 2d 382, 233 P. 2d 914, where the court said (105 Cal. App. 2d at 390-392):

". . . Having so determined, the trial court was thereby of necessity required to formulate a practical decree which would restrain respondent from maintaining a nuisance and yet permit the operation of its plant with as little interference as was reasonably practicable. This we think the trial court clearly attempted to do and succeeded in doing.

". . . The trial court, while finding that a nuisance was being maintained, also found impliedly that the restriction imposed by the decree would eliminate the nuisance and that was all to which the appellants were then entitled. If further increase of cement production shall lead to a greater total volume of dust and gases, so that 13 per cent thereof would be injurious, the court will be open to entertain a motion to extend the restrictions and adapt them to the new conditions. We do not understand the court's decree to adjudge that respondent has something in the nature of an easement for the deposit upon the appellants' lands of 13 per cent of the total amount of dust and gases generated in the conduct of its business, but rather that the court has taken the situation as it found it and undertook to impose workable restrictions that would eliminate the injury for the present. There is nothing in the record that would require any change in that decree in the present or in the near future. The court of course retains jurisdiction over the cause to modify its decree from time to time to fit changing conditions."

Anticipatory Nuisance

It is significant to note that as early as 1868 in the case of *Ross* v. *Butler,* 19 N.J.E. 294, a request for an injunction to prevent the erection of a lawful business which allegedly would result in a public nuisance was granted even before the nuisance actually came into existence. The court in that case said that when the prosecution of a business in itself lawful, in the neighborhood of a dwelling house, renders the enjoyment of it materially uncomfortable by the smoke or cinders or noise or offensive odors produced by such business, although in no degree injurious to health, the carrying on of such business there is a nuisance.

So too in the case of *Shaw* v. *Salt Lake County,* 119 Utah 50, 224 Pac. 2d 1037 (1950) it was established that private persons had the right, despite sovereign immunity, to enjoin a county in its governmental capacity, from erecting a hot asphalt plant which plant the court found would cause a dust nuisance when completed and put into operation.

Coming to the Nuisance

This concept is based on the early common law doctrine that he who builds his house near a known and existing nuisance must take the consequences. It was first announced in *Rex* v. *Cross* (1826) 2C. & P. 483, 172 Eng. Rep. 219 (subsequently overruled in England).

The rule of *Rex* v. *Cross* was adopted by the Supreme Court of Oregon in *East St. Johns Shingle Co.* v. *Portland* (1952) 195 Ore. 505, 246 P. 2d 554, at least as applied to the limited situations of that case, where a public body is defendant and the nuisance arises from the performance of a governmental function (sewage disposal). The case is criticized in a note by Cassius Kirk, Jr., in 41 Calif. Law Review 148 (Spring, 1953).

A company charter authorizing the manufacture of animal matter into a fertilizer is not a contract guaranteeing in the locality originally selected, exemptions from the exercise of the police power of the state, however serious the nuisance might become in the future by reason of the growth of population around it. *Northwestern Fertilizing Co.* v. *Village of Hyde Park,* 97 U. S. 659, 24 L.Ed. 1036.

See also: *Mahone* v. *Autry* (1951) 55 N. Mex. 111, 227 P. 2d 623.

In *City of Rochester* v. *Charlotte Docks Co.,* (1952) 114 N. Y. Supp. 2d 37, 72-73, the case against the rule of *Rex* v. *Cross, supra,* is clearly stated:

". . . A continuation of the nuisance is regarded as a new nuisance. It is this principle which gives a party who builds on his own property beside a nuisance, previously erected, a right to have the nuisance abated.

"Our decision is not influenced by the fact that quite a number of plaintiffs became owners of the property after the alleged nuisance existed for a number of years, or that, even knowing it was so affected, they still persisted in buying property in the area . . .

"The right of habitation is superior to the right of industry or trade . . . 'If population, where there was none before, approaches a nuisance, it is the duty of those liable at once to put an end to it . . .'

"It matters not that the brick-yard was used before plaintiffs bought their lands or built their houses. (citing cases.) One cannot erect a nuisance upon his land adjoining vacant lands owned by another and thus measurably control the uses to which his neighbor's land may in the future be subjected. He may make a reasonable and lawful use of his land and thus cause his neighbor some inconvenience, and probably some damage which the law would regard as *damnum absque injuria.* But he cannot place upon his land anything which the law would pronounce a nuisance, and thus compel his neighbor to leave his land vacant, or to use it in such way only as the neighboring nuisance will allow . . ."

Recent cases dealing with air pollution control ordinances have considered the subject of criminal intent as an element of the offense.

Intent Not Necessary to Violate Statute or Ordinance

"The criminal intent or *mens rea* essential to a conviction in the case of true crimes need neither be alleged or proven with respect to violations of municipal ordinances which forbid the commission of certain actions contrary to the general welfare and makes them *malum prohibitum.* Proof or admissions of the doing of the forbidden thing, regardless of intent, good faith, or willfulness, must bring a conviction." *People* v. *Consolidated Edison Co. of N. Y., Inc.,* 116 N.Y.S. 2d 555.

In *People* v. *Alexander,* Unreported, Appellate Department, Superior Court, Los Angeles County, California, CR A 2709, (1951) the defendant was charged with violating provisions of section 24242 of the Health and Safety Code of the State of California, for discharging air contaminants into the atmosphere on 2 separate occasions.

The court in that case held that an instruction rendered by the trial court was correctly given as follows:

"It is the actuality and not the guilty intent that determines guilt. Intent is not an element of the offense defined in Health and Safety Code, sec. 24242."

Damage Necessary to Sustain An Action to Enjoin a Common Law Nuisance

In *Hofstetter* v. *Myers* (1951) 170 Kans. 564, 228 P. 2d 522, 24 A.L.R. 2d 188, the trial court enjoined as a nuisance the operation of an asphalt plant *at such times and manner that the dust and dirt coming therefrom will injure, molest or interfere with the plaintiffs in the peaceable, quiet enjoyment of their property.* The evidence showed that the dust reached plaintiffs only when the wind was from the southwest, was not accompanied by soot, smoke, odors or fumes, was the same as the dust from unpaved roads in the vicinity and merely *inconvenienced* plaintiffs, who had built homes in the area notwithstanding the presence of 2 railroads and the municipal garbage dump. (However, these home were built *before* defendant's asphalt plant.) The Kansas Supreme Court reversed the judgment, saying (24 A.L.R. 2d at 193-194):

"While the word 'nuisance' is perhaps incapable of precise definition, yet in general it is held to be something which interferes with the rights of citizens, whether in person, property, or enjoyment of property, or comfort. It has also been held to mean an annoyance, and, in its broadest sense, that which annoys or causes trouble or vexation, that which is offensive or noxious, or anything that works hurt, inconvenience or damage. (Citation). What may or may not constitute a nuisance in a particular case depends upon many things, such as the type of neighborhood, the nature of the thing or wrong complained of, its proximity to those alleging injury of damage, its frequency of continuity, and the nature and extent of the injury, damage or annoyance resulting. Each case must of necessity depend upon its own particular facts and circumstances.

"As a general proposition it may be said that dust which substantially interferes with the comfortable enjoyment of adjacent premises constitutes a nuisance, provided it is sufficient to cause perceptible injury to persons or property. On the other hand, a reasonable amount of dust in a manufacturing community or industrial district does not necessarily constitute a nuisance even though it may cause some annoyance, and this is particularly true where the dust caused by the operation of a business is only occasional and the resultant injury slight. In other words, a given amount of dust in one locality well might be considered and held to be a nuisance, and not so in others, all depending upon the particular facts and circumstances . . ."(2)

The case of *McIvor* v. *Mercer-Fraser Co.,* (1946) 76 Cal. App. 2d 247, 172 Pac. 2d 758, involved an excavation which removed lateral support of plaintiff's land, but was decided on the basis of public nuisance, citing air pollution control cases. The court said at pp. 253-254:

"It was not necessary for respondents to show actual physical damage to their property . . . The deprivation by defendants of plaintiffs' right to enjoy their property to the full constituted a partial eviction . . . The fact that it was only partial does not deprive respondents of their right of action. As the court stated in *Judson* v. *Los Angeles Gas Co., supra,* at page 172: 'It is surely no justification to a wrongdoer that he takes away only one twenty-eighth of his neighbor's property, comfort or life.'

". . . mere apprehension of injury from a dangerous condition may constitute a nuisance where it interferes with the comfortable enjoyment of property (46 C.J. sec. 50, p. 680), and that the injured party need not seek an abatement of the nuisance but may sue for damages."

Alonzo v. *Hills* (1950) 95 Cal. App. 2d 778, 214 P. 2d 50, is not in point on its facts, being a suit for damages from blasting (for which a much higher standard of care is usually required), but the court reaches its conclusion as to damages on the basis of air pollution cases. The court said at pp. 787-788:

". . . The recovery for such invasion of his rights in the real property to which the owner-occupant is entitled includes discomfort and annoyance . . .

". . . The amount of the recovery for discomfort and annoyance is left to the sound judgment and discretion of the trier of facts without necessity of specific evidence as to such amount."

Injury to the public must be more than trivial, fastidious or offensive to esthetic senses. There must be some material damage to the public that is more than trivial, fastidious, or offensive to the esthetic senses, to render smoke a nuisance.

In the case of *Tuebner* v. *California Railway Company,* 66 Cal. 171, 4 Pac. 162, 1164 (1884), involving a private nuisance, the court quoted with approval from Cooley on Torts, as follows:

"'If the smoke or dust, or both, that arises from one man's premises and passes over and upon those of another, causes perceptible injury to the property, or so pollutes the air as sensible to impair the enjoyment thereof, it is a nuisance. But the inconvenience must be something more than mere fancy, mere delicacy, or fastidiousness; it must be an inconvenience materially interfering with the ordinary comfort, physically, of human existence, nor merely according to elegant and dainty modes and habits of living, but according to plain, sober, and simple notions.'"

The Ringelmann Chart

While the Ringelmann Chart has been commonly used in ordinances and elsewhere as a measure of smoke emission for half a century, few cases referred to it and none actually approved its use. Since 1947 the courts have been more generous in their notice of it. The Appellate Department of the Los Angeles County Superior Court (California) approved the use of the chart in *People* v. *International Steel Corp.* (1951) 102 Cal. App. 2d Supp. 935, 226 P. 2d 587, at 938-9, stating:

"We think it is equally permissible for a statute to refer to and adopt, for description of a prohibited act, an official publication of any United States board or bureau established by law, such as the United States Bureau of Mines. The publications of that bureau are as readily available for examination by those seeking information on the effect of the statute as were the statutes and regulations, references to which were approved in the cases just cited. It is no more necessary here than it was in those cases that provision be made for free or other public distribution of the matter referred to. The courts take judicial notice of the official acts of the Bureau of Mines . . . and private citizens who are concerned with them are also charged with notice of them."

The court then proceeds to discuss the use of the Ringelmann Chart in detail, and holds that inspectors trained in the use of the chart are experts and may testify as such to the Ringelmann number of a particular smoke emission, without using a chart (just as a police officer could testify to the length of a skid mark without actually measuring it with a tape measure or ruler).

Other recent cases approving the use of the Ringelmann Chart are: *Board of Health of Weehawken Township* v. *New York Central Railroad* (1950) 4 N.J. 293, 72 A. 2d 511, 512; *Board of Health of Weehawken Township* v. *New York Central Railroad* (1952) 10 N. J. 294, 90 A. 2d 729, 735; *Penn-Dixie Cement Corp.* v. *City of Kingsport* (1949) 189 Tenn. 450.

Multiple Sources of Pollution

With the growth of cities and the multiplication of industrial plants more and more cases arose where there were several contributing sources of pollution making it difficult to prove any defendant guilty of a nuisance. In some cases no one factory was responsible for enough pollution to constitute a nuisance, but the total contribution of two or more sources of pollution was a nuisance. Recent cases have found those responsible for the various contributions to be joint tort feasors, or at least not in a position to object if the court divides the damages between them as best it can.

In *Ingram* v. *City of Gridley* (1950) 100 Cal. App. 2d 815, 224 P. 2d 798, the court said (at pp. 823-4):

"But it is also contended that no award of damages could be given against the appellants because the damages were not apportioned, the appellants claiming that damages in a case such as this must be apportioned among the creators of the nuisance and if that cannot, from the nature of the case, be done, damages cannot be awarded jointly against all. We think this contention likewise cannot be sustained. The record here reveals that each of the appellants, with full knowledge of the acts of the others, and in the face of repeated requests for a cessation of the acts which created the nuisance, continued to act and by their acts to create the nuisance complained of and treated

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with each other concerning the matter to such an extent that they should be held to be joint tort feasors, each liable for the full damage . . ."

In *Permanente Metals Corp.* v. *Pista* (CCA 9, 1946), 154 Fed. 2d 568 at 570, the court reached a similar decision, and analyzed *California Orange Co.* v. *Riverside Portland Cement Co.*, 50 Cal. App. 522, 195 Pac. 694, as follows:

". . . the court said that if it is impossible to distinguish between the damage arising from injury attributable to the defendant and damage which has another origin, the trier of the facts should be left to make from the evidence the best possible estimate. The court pointed to evidence showing 'that plaintiff's grove, though not subject to any greater damage from the elements than other groves situated outside the zone of falling cement dust, did not produce as did the groves similarly situated outside the dust zone.' The showing was thought sufficient to support the award of damages against the defendant."

For similar holdings, see *International Agr. Corp.* v. *Abercrombie,* 184 Ala. 244, 63 So. 549, 49 L.R.A., N.S. 415; *Learned* v. *Castle,* 78 Cal. 454, 461, 18 P. 872, 21 P. 11, 13; *Hanlon Drydock etc. Co.* v. *Southern Pacific Co.,* 92 Cal. App. 230, 268 P. 385.

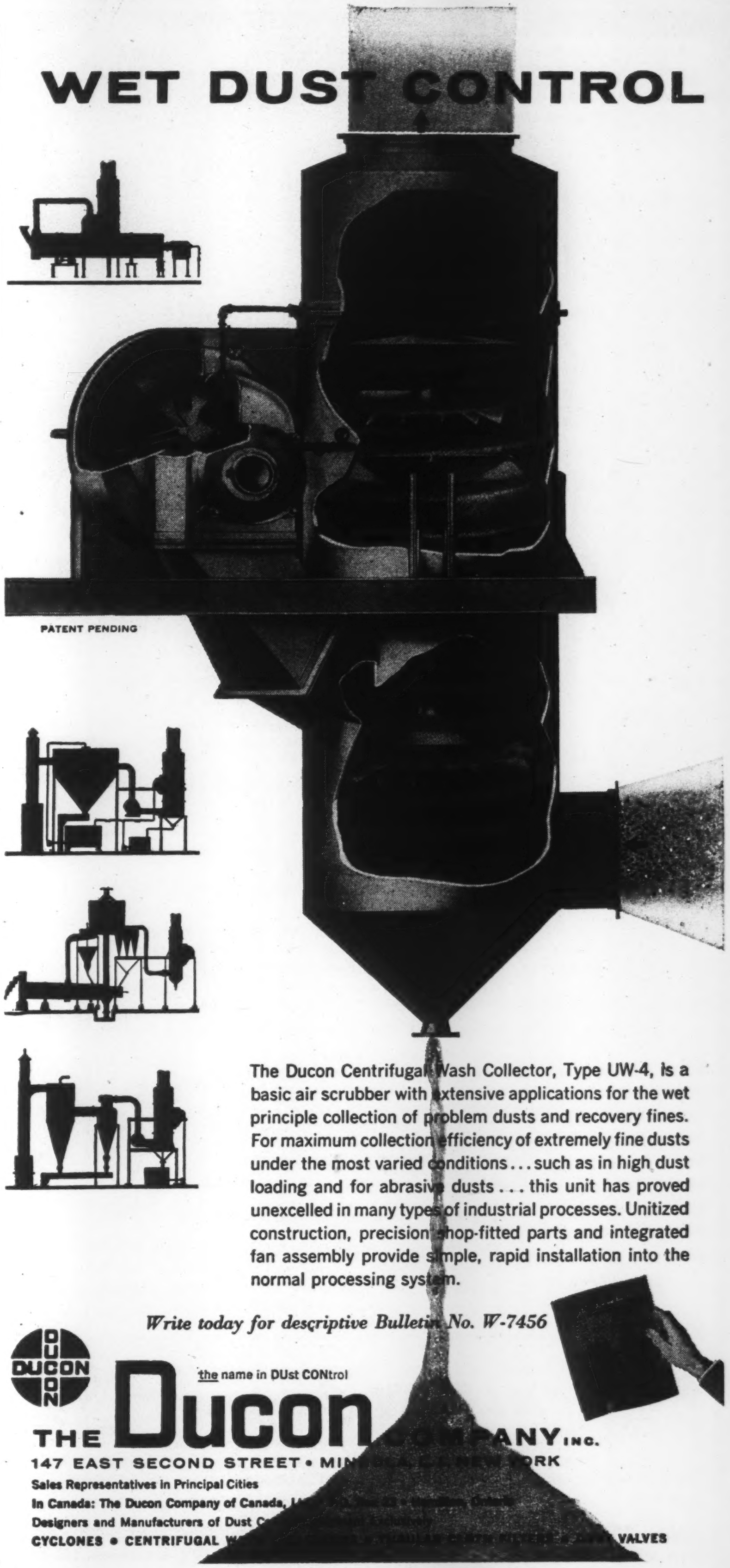
Reasonable Use of Property and Substantial Compliance With Ordinance Regulations

At an earlier point in this discussion, mention was made of the decision in the case of *People* v. *Detroit White Lead Works, supra,* which held that whenever a business becomes a nuisance it has to give way to the rights of the public even though nothing is done which is not a reasonable and necessary incident to the business.

In support of the rule laid down in the *Detroit White Lead* case the court in *Moses* v. *United States, supra,* said:

"That there may be no smoke-consuming appliances that will, under all circumstances, prevent the nuisance it is not a matter of relevancy. The facts concerning them were presumably within the knowledge of Congress also when it took action; and no provision has been made for their use. The use of smokeless fuel instead may have been expressly contemplated."

Several cases involving private nuisances notably *Elliot Nursery* v. *Duquesne Light,* 281 Pa. 166, 126 Atl.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345, 37 A.L.R. 793; *Price* v. *Carey Manufacturing Co.*, 310 Pa. 557, 165 Atl. 849 (1933); *Downs* v. *Greer Beaty Clay Co.*, 29 Ohio C.C. 328, 58 A.L.R. 1226 (1905), held that the business involved were not guilty of violations because they were using the best known modern appliances to prevent smoke and fumes.

A fair test as to whether a business constitutes a nuisance is the reasonableness or unreasonableness of conducting the business complained of in the particular locality and under the circumstances of the case; and where the use of the property is not unreasonable, it will not as a rule, be enjoined, nor can a person complaining thereof recover damages. *Reber* v. *Illinois Central Railroad Co.*, 161 Miss. Rep. 885, 138 So. 574 (1932).

Where a bill was brought by property owners to enjoin defendants from maintaining a nuisance by the emission of obnoxious fumes and odors, the court in *De Blois* v. *Bowers*, 44 Fed. 2d 621, (1930), stated:

"Mere discomfort caused by such conditions without injury to life or health, cannot be ruled as matter of law to constitute a nuisance. Each case must depend upon its own fashion and no rule can be formulated which will be applicable to all causes.

"The question whether the defendants have done everything reasonably practicable to avoid the cause of offense is important. Reasonable care must be used to prevent annoyance and injury to other persons beyond what the fair necessities of the business require."

In the more recent case of *People* v. *Oswald*, 116 N.Y. Supp. 2d 50 (1952), where the defendant was prosecuted for violation of provision of the Administrative Code of the City of New York prohibiting the emission of dense smoke, the defendant was held not to be guilty since he had done everything possible to comply with the regulations promulgated under the code. In so holding, the court said:

"This legislation is regulatory in character and must be interpreted in the light of its necessity and the purpose to be accomplished. It is *malum prohibitum* and regardless of the efforts made by any individual to avoid a violation of the law or regardless of the intent if the prohibited action occurs that in and of itself is sufficient to constitute a violation. But this rule is subject to reason and the court must not close its eyes to obvious facts. The law does not seek to compel a man to do that which he cannot possibly perform. *Walden* v. *City of Jamestown*, 178 N.Y. 213, 217, 70 N.E. 466, 467.

"A reasonable interpretation should be made and if the adduced proof shows that a defendant has complied with the literal requirements of the law as nearly as it is practicable to do so under the prevailing circumstances, and that he has adopted the best devices presently known to all, then the letter and spirit of the legislation has been complied with. In interpreting statutes sense must be brought out of words used. *McCluskey* v. *Cromwell*, 11 N. Y. 583."

Perhaps the differing views on whether use of the best device is a defense can be rationalized as each depending upon the gravity of the problem in a given location. Assuming a situation in which air pollution has become so severe as to cause great annoyance and damage, or perhaps personal injury or death, there can be little doubt that by adopting the best control devices known a defendant could not shield himself from liability, civil or criminal.

Summary—The Next Fifty Years

We have seen the progress in the development of air pollution law during the past half century. Against the backdrop of the state of the law existing in 1907, the last 50 years appears to have been a period of refinement rather than revolution. Out of the decisions that fit together nicely, fit only roughly, leave yawning gaps, or directly conflict, the air pollution lawyer must derive a concept of what the law is, in order to guide himself and his client over the troublesome road ahead. Generally speaking, the law of air pollution has seen these major developments since 1907.

(1) The doctrine of nuisance has followed in the course of urban and industrial development.

(2) The control of air contamination by the use of strict statutory and administrative regulations has become quite popular.

(3) The courts have adhered fairly rigidly to the letter of the new police regulations. The way of the transgressor has become increasingly difficult.

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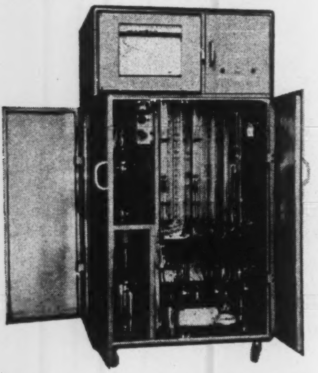

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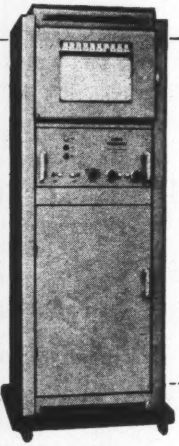

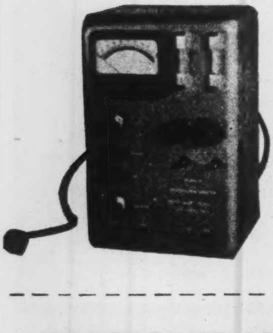

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fluid boundaries of the law. We can prognosticate that there will be no upheavals which will destroy or seriously alter the great concepts upon which common law and constitutional law are based.

The area of our crystal ball which is darkest, however, is that portion wherein lies the answer to the question: *In which direction will the police power move?* That question will largely depend on how quickly and economically scientists and engineers and industry can solve the practical problems of air pollution control. Police regulations will follow closely on the heels of technical development.

We can already see clearly one factor involved in the future development of the police power. That factor is public indignation. The free citizen, now enjoying an otherwise miraculous standard of living, cannot, will not, and should not be forced to undergo the exquisite tortures inflicted upon him constantly by metropolitan living. In some geographic areas, air pollution or *smog* is not a serious concern to him—not yet. In other locations air contamination is rated the cardinal concern. It will suffice to predict here that as and if the air contamination problem becomes more serious, new police regulations will follow, and these regulations, unless palpably capricious, will be upheld by breathing judges.

Acknowledgements

Acknowledgment is given to David D. Mix and C. George Deukmejian, Deputies County Counsel of the County of Los Angeles, for valuable assistance rendered in the research of the legal material used in this paper.

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1 Ralph H. German. Regulation of Smoke and Air Pollution in Pennsylvania. 10 U. of Pitt. L.R. 493, (May, 1949). This article defines some of the technical words used in such ordinances, gives some interesting history and discusses the Pittsburgh Ordinance (modeled after that of St. Louis). A companion article, *Technological Factors in Relation to Some Legal Aspects of Smoke Control,* by Henry F. Gebley, in the same issue of the law review at page 505, gives a model form of ordinance for control of fly ash. The form of the decree in *Guttinger* v. *Calavaras* Co., 105 Cal. App. 2d 383, 233 P. 2d 914, at 384-5, should be consulted in writing an ordinance to control cement dust.

2 The American Law Reports annotation (at pp. 194-234 of 24 A.L.R. 2d) following the report of this case collects the cases on the subject of *Dust as Nuisance,* including some on the interesting question of anticipatory nuisance (at p. 204).

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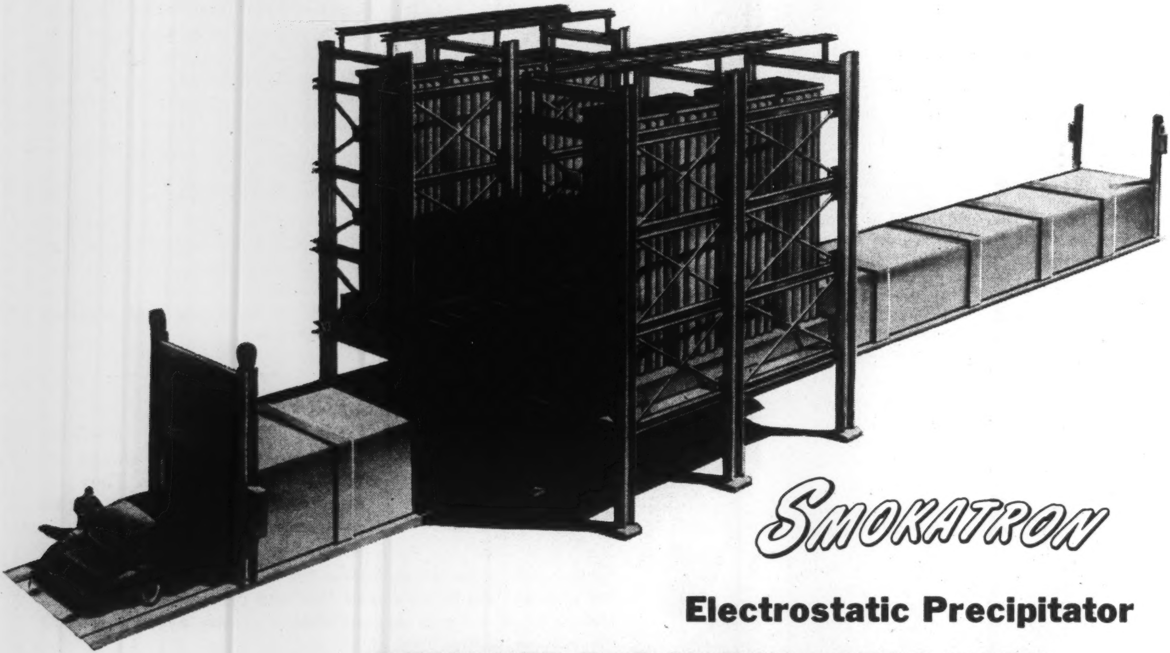

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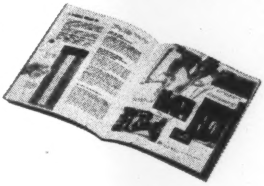

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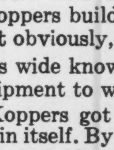

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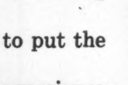

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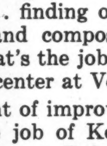

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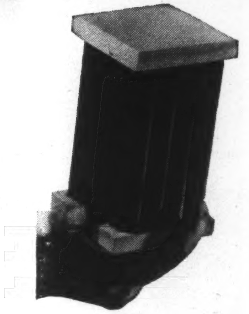

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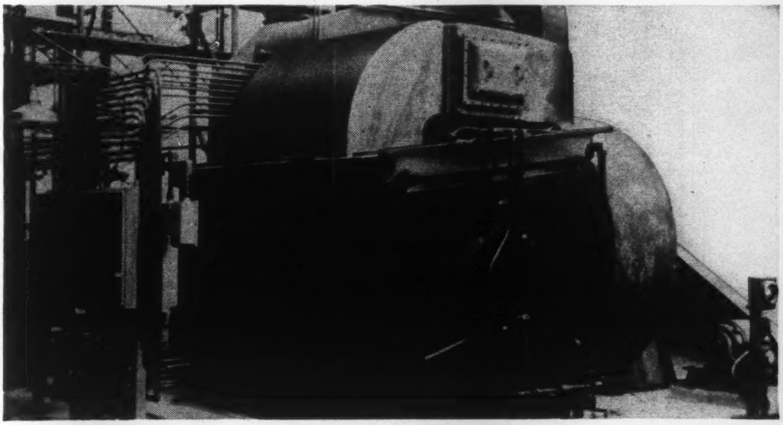

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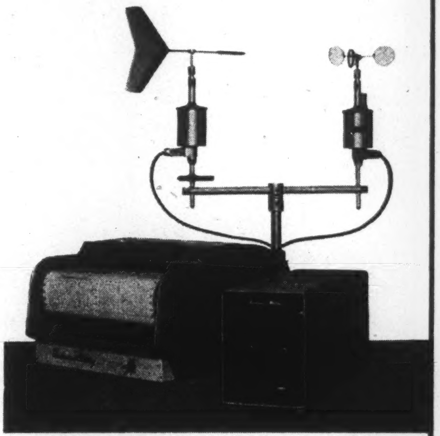

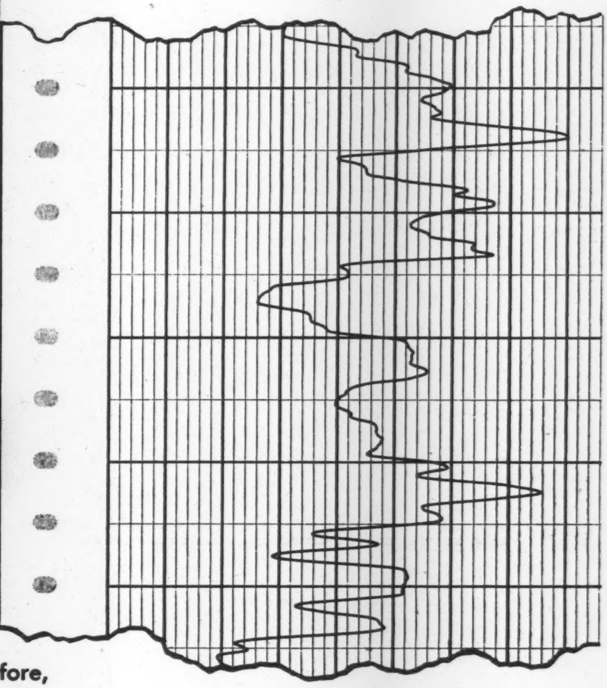

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